# INSTITUTE NOTES.

## MAY 1940.

### NEW MEMBERS.

The following elections have been made by the Council in accordance with the By-Laws, Section IV, Para. 7.

Elections are subject to confirmation in accordance with the By-laws, Section IV, Pars. 9 and 10.

*As Fellows.*

| | |
|---|---|
| MOND, Albert Levy | London. |
| EISNER, John Hans | Ellesmere Port. |

*As Members.*

| | |
|---|---|
| GASCOIGNE, George Norman | London. |
| SCHARGES, Walter Herbert | Cape Town. |
| TEMPLE, George Edward Maskell | Iran. |
| TOKAYER, Oscar | London. |

*Transfer to Member.*

| | |
|---|---|
| HIGGS, Percival George | Egypt. |

*As Associate Members.*

| | |
|---|---|
| ALLCARD, Harry Ganly | Manchester. |
| BRADFORD, Job Ronald Tremellen | London. |
| CARTER, Edward Howard | Willerby. |
| FORSTER, Denis Williams | Warrington. |
| GREIG, Alan Lancelot | London. |
| HILTON, John Sydney | Leeds. |
| KENYON, Harold Frederick | Cambridge. |
| MARSHALL, Edward Thomas | H.M. Navy (R.N.R.). |
| PARTRIDGE, William Arthur | London. |
| ROGER, Arthur | Warrington. |

*As transfer to Associate Member.*

| | |
|---|---|
| LISLE, Brian Orchard | New York. |

*As Students.*

| | |
|---|---|
| AUSTIN, John Martin | Birmingham. |
| BUXTON, Geoffrey | Birmingham. |
| CHEETHAM, Harry Alan | Birmingham. |
| CLARKE, Geoffrey Jardine | London. |
| CUDE, Arthur Leslie | Birmingham. |
| CHIVERS, Harold Victor | Birmingham. |
| GRUNBERG, Leander | Birmingham. |
| HAWKES, John Cecil | Birmingham. |
| METCALFE, John Leslie | Birmingham. |
| NEILSON, Ian McIntosh | Birmingham. |
| SHACKELL, Douglas Ashton | Birmingham. |
| SIMPSON, Alan Murray | Birmingham. |
| TONGE, Peter | Birmingham. |
| WISEMAN, Kenneth William | Birmingham. |
| WOOD, George Frederick | Birmingham. |

The following have been transferred to Fellowship under the temporary regulations in force for 1939 :—

MALHERBE, Gideon John. MACLEAN, Thomas Traill.
TITCHMARSH, George Henry.

## CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Fellow, Member, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

AGOSTINI, Pierre Leon, Engineer, c/o Trinidad Leaseholds, Ltd., Forest Reserve, Trinidad, B.W.I. (*J. L. Harris ; F. S. Tindall.*)

BROWN, Norman Fraser, Fields Chief Engineer, Indo-Burma Petroleum Co., Ltd., Rangoon, Burma. (*C. F. C. Moore ; A. E. Day.*)

COOPER, Arundel David, Chemist, c/o The Anglo-Egyptian Oil Co., The Refinery, Suez, Egypt. (*J. Kewley ; W. P. Hodgson.*) (*Trans. to Fellow.*)

PACHACHI, Nadim, Student, Ministry of Economics, Baghdad, Iraq. (*S. E. Coomber ; G. D. Hobson.*) (*Trans. to Associate Member.*)

PEASE, Sherman Levi, Engineer (*U.B.O.T.*), 626, 16th Avenue Southeast, Minneapolis, Minnesota, U.S.A. (*G. S. Taitt ; R. F. Connock.*)

PRUTTON, Carl F., Ph.D., Professor of Chemical Engineering, Case School of Applied Science, Cleveland, Ohio, U.S.A. (*W. Miller ; J. F. T. Bowles.*)

SUTER, Hans H., Geologist, c/o Trinidad Leaseholds, Ltd., Pointe-a-Pierre, Trinidad, B.W.I. (*B. G. Banks ; H. C. H. Thomas.*)

TULLY, James, Engineer, Aln House, Thropton, Northumberland. (*C. Dalley ; H. W. Barnes.*)

ARTHUR W. EASTLAKE,
*Honorary Secretary.*

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*Kindly mention this Journal when communicating with Advertisers.*

Vol. 26. No. 199. May 1940.

# THE SYNTHESIS OF LUBRICATING OILS BY CONDENSATION REACTIONS.*

## PART II.—THE ENGINE TESTING OF SYNTHETIC LUBRICATING OILS.

By W. R. Wiggins, Ph.D., T. G. Hunter, Ph.D., M.Inst.Pet., and A. W. Nash, M.Sc., F.Inst.Pet.

The engine service characteristics of two synthetic lubricating oils were evaluated by means of an engine test. The oils examined were :—

(1) Synthetic oil $S/_1$ made by the condensation of chlorinated paraffin wax with benzene using an Al catalyst.
(2) Synthetic oil $S/_2$ made by the condensation of chlorinated paraffin wax with benzene using an $AlCl_3$ catalyst.

The service characteristics evaluated were :—

(1) Engine wear.
(2) Oil consumption.
(3) Carbon deposits.
(4) Condition of oil in crank-case.

### Engine Wear.

Engine wear can be evaluated by measuring the change in weight of piston rings, by measuring the increase in diameter of cylinder bores, and by measuring chemically the iron carried away by the lubricant. For the engine tests described in this paper all three methods were employed. The measurement of wear by ascertaining the increase in iron content of the lubricating oil was first suggested by Langdon,[1] and has been employed by Everett and Stewart,[2] and by Boerlage and Gravensteyn.[3] It has been further developed by Merrill, Moore, and Bray,[4] who expressed the increase in iron content of the lubricating oil as a wear index. In this test the wear index, representing the amount of wear in milligrams of iron per 1000 miles of operation, was expressed by the following formula :—

$$W = (C + D)(I_2 - I_1) + R(I_1 + I_2)\frac{567{,}000G}{(B - A)}.$$

where $W$ = wear index, in mgms. of iron per 1000 miles.
$A$ = speedometer reading, in miles, when first oil sample taken.
$B$ = speedometer reading, in miles, when second oil sample taken.
$C$ = original volume of oil, quarts.
$D$ = final volume of oil, quarts.
$R$ = volume of make up oil, quarts.
$G$ = density of original oil, lb./gallon.
$I_1$ = per cent. iron in oil sample at $A$.
$I_2$ = per cent. iron in oil sample at $B$.

* Paper received 6th September, 1939.

In deriving this formula it is assumed that :—

(*a*) Oil consumption is a straight-line function of miles of operation.
(*b*) Iron wear is a straight-line function of miles of operation.
(*c*) Oil consumed carries with it a proportional amount of iron.

It is shown in the following section, under the heading "Oil Consumption," that assumption (*a*) is for all practical purposes correct over runs of about 1500 miles.

In Fig. 1 the wear expressed both as wear index and piston-ring wear for

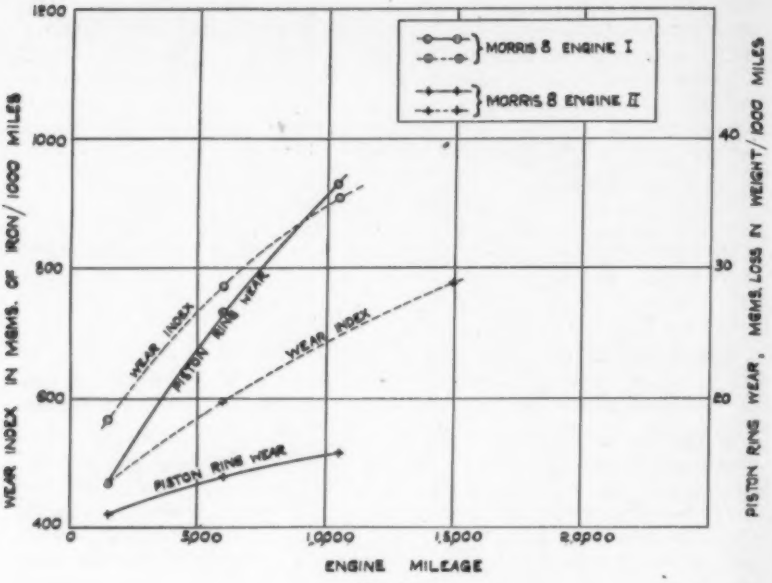


FIG. 1.

two different Morris 8 engines, run at constant speed for test runs of 1500 miles, using the reference oil, is plotted against engine mileage. Bench tests were employed to obtain this and all other data detailed in this paper and the mileage figures quoted here were derived from a speedometer attached to the gear-box of the engine unit. It will be observed that over runs of 1500 miles wear is practically a straight-line function of miles operated. Assumption (*b*) is therefore justifiable for runs up to about 1500 miles.

Wear index gives dependable results for the comparison of the wear properties of several oils if all tests are run under standard engine conditions and the oils evaluated by comparison with a reference oil. The wear data given in this paper have all been referred to a selected reference

oil, and are really relative wear figures. They have been calculated by the following expression :—

$$\text{Relative Wear} = \frac{Tw}{Rw} \times 100$$

where $Tw$ = wear of test oil.

$Rw$ = wear of reference oil at the same engine mileage as that at which the wear value, $Tw$, of the test oil was obtained.

Since, as has been shown in Fig. 1, wear is a function of the miles the engine has operated, the value $Rw$, whether loss in weight of piston rings, increase in diameter of cylinder bore, or wear index, is easily obtained by interpolation from a plot of reference oil wear against engine mileage. The simplest way of obtaining satisfactory figures for interpolation is to carry out alternate engine tests with reference and test oils as follows : reference oil, test oil, reference oil. A less satisfactory but somewhat more economical procedure is to carry out two test oil runs between reference oil runs as follows : reference oil, test oil 1, test oil 2, reference oil. The latter method was the method adopted for the tests described in this paper. The reference oil employed was a proprietary brand of motor oil.

## Oil Consumption.

Oil consumption as related to direct actual consumption in the engine is dependent on four main factors :—

(1) Engine speed.
(2) Engine design.
(3) Engine changes due to wear.
(4) Oil characteristics—namely, viscosity and volatility, oil consumption decreasing with increasing viscosity and decreasing volatility.

In the engine tests described in this paper factors (1) and (2) above were eliminated as far as possible by using the same engine throughout the tests, run under constant engine conditions. Oil consumption as ascertained from the tests is therefore consumption as affected by factors (3) and (4). Factor (3) engine wear for a given oil was found to be a function of miles operated, and oil consumption for a given oil in a given engine run at constant speed should also be some function of miles operated. In Fig. 2 oil consumption of the reference oil in two different Morris 8 engines operated at constant speed is plotted against mileage. It will be observed that, while the function is not linear, it may be taken to be so without much error over runs of about 1500 miles.

In order to eliminate, therefore, the effect of engine changes due to wear or oil consumption, a relative oil-consumption figure has been employed, in which the actual oil consumption of the test oil at a known engine mileage is compared with the oil consumption of the reference oil at the same engine mileage. This latter value is obtained from a plot of the oil consumption of the reference oil against engine mileage, the reference oil-consumption data being obtained from reference oil tests run at regular intervals throughout a series of experiments.

The relative oil consumption measured is therefore, as near as can be obtained, a function of lubricating oil characteristics.

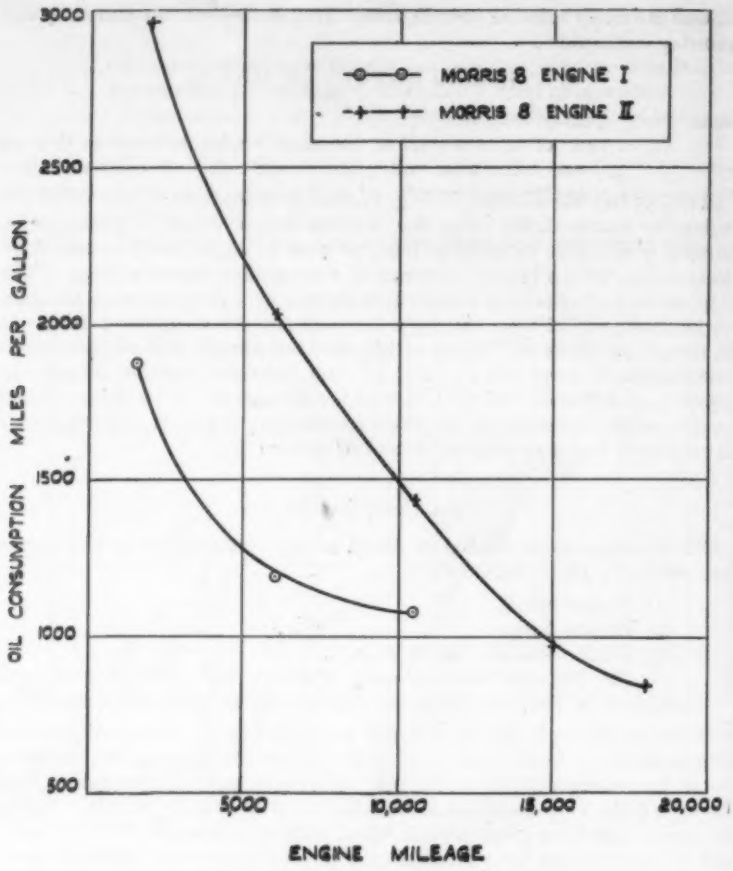


FIG. 2.

## CARBON DEPOSITS.

The more important factors which govern the formation of carbon deposits in petrol engines are :—

(1) Engine design.
(2) Engine running conditions, temperature, speed, load, and miles operated.
(3) Amount of dust in air.
(4) Air–fuel mixture ratio.
(5) Characteristics of fuel.
(6) Oil consumption.
(7) Engine condition.
(8) Characteristics of lubricating oil.

Throughout the tests described here factors (1) to (5) were maintained approximately constant, and hence their effect on the carbon deposits may be considered negligible. Carbon deposits vary with oil consumption, and will be considered here on the basis of carbon deposit per volume of oil consumed.

In Fig. 3 the carbon deposit per volume of oil consumed for two different Morris 8 engines run at constant speed for test runs of 1500 miles using the reference oil is plotted against engine mileage, and is a function of miles

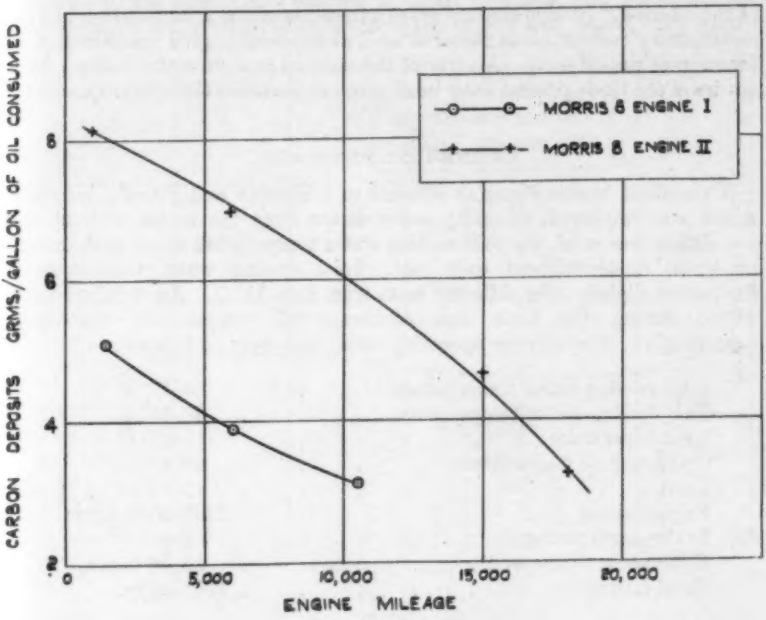


FIG. 3.

operated. As in the case of the wear and oil-consumption figures, carbon deposits have been expressed as relative to the reference oil consumption at the same engine mileage.

Comparison on this basis will therefore indicate to a large extent the differences due to the characteristics of the different lubricating-oil samples tested.

## CONDITION OF OIL IN CRANKCASE.

Changes in characteristics of crankcase oils during service appear to depend considerably on the type of engine, its condition, and manner of operation. Keeping engine conditions constant, as has been done in the present series of tests, demonstrates approximately crankcase changes as a function of new oil characteristics.

The following tests of used crankcase oils give some indication of their service changes :—

(1) Viscosity.
(2) Sludge content.
(3) Acidity.

Viscosity change indicates the accumulation or non-accumulation of soluble polymerized products and residues from cracking and partial burning of the oil and, under constant engine conditions, is a characteristic of the oil used. Sludge content gives a measure of the accumulation of fine sedimentary carbonaceous material and, at constant engine conditions, is a function of the oil used. Acidity of the used oil is of doubtful value. The nature of the acids present may be of more importance than their quantity.

## Engine-Test Procedure.

A standard Morris 8 engine coupled to a Heenan and Froude dynamometer was employed. Cooling water direct from the mains without recirculation was used, the exit cooling water temperature being maintained at 40–50° C. throughout each test. Inlet cooling water temperatures fluctuated slightly over different tests from 6 to 11° C. Air temperatures varied during the tests and crankcase oil temperature fluctuated accordingly. The average operating conditions were as follows :—

| | |
|---|---|
| Inlet cooling-water temperature | 6–11° C. |
| Exit cooling-water temperature | 40–50° C. |
| Air temperature | 10–27° C. |
| Crankcase oil temperature | 40–63° C. |
| Load | 12–15 lb. |
| Engine speed | 2450–2550 r.p.m. |
| Brake horse power | 7·2–8·3 |
| Equivalent road speed | 35–36 m.p.h. |
| Total mileage | 1500 miles. |

Air and cooling-water temperatures were measured by mercury in glass thermometers. Crankcase temperatures were measured by a thermocouple inserted in an internal sheath welded into the crankcase. As far as possible, the oil level in the crankcase was maintained at the maker's recommended level, make-up oil being added gradually as required. Oil consumption was determined from the measured volumes of initial, final, and make-up oils.

In order to disturb the engine as little as possible, only the top ring of each piston was weighed at the end of each test, as the greatest loss in weight occurs in the top ring, and care was taken to replace the same ring on the same piston on reassembling. By not disturbing the other rings, large engine changes were hoped to be avoided to a certain extent. Cylinder bore measurements were taken at the top of each cylinder, two measurements being taken by an internal micrometer, one parallel to the crankshaft and the other at right angles to it. This allowed for any tendency in the cylinders to wear oval. Check bore measurements were also taken at the bottom of the cylinder in a direction at right angles to the crankshaft.

At the end of each test the engine-head was removed, and all carbon deposits on the engine-head and on the top of the piston were detached with a blunt scraper and weighed.

At the finish of each test the oil was drained out of the crankcase while still hot. The crankcase was removed, washed with kerosine, and wiped completely dry. The oil pump was then submerged in a beaker containing 300 c.c. of the reference oil, and the engine motored over with the starter. This oil was sucked up by the pump, passed through the engine oiling system and discharged from the various oil-discharge holes to waste. Any oil retained in the engine was allowed to drain to waste, and the crankcase was not replaced until all oil-drips from the engine had ceased. By means

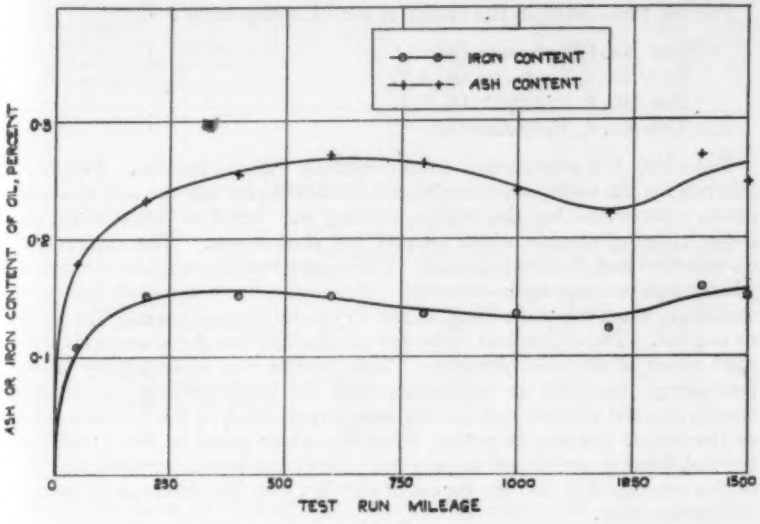


Fig. 4.

of this procedure contamination of the oil samples taken for analysis at the beginning of the test with oil from the previous test was reduced to a minimum. Oil samples for analysis were taken from the pump delivery line by means of a T-piece with sampling cock attached. About 100 c.c. of oil were discharged through the sampling cock and returned to the sump, then approximately 10 gm. of oil were sampled directly into a tared porcelain crucible, samples being taken in duplicate. Samples were taken every 100 miles in the case of the first oil tested—namely, the reference oil. It was, however, found rather difficult to keep up to date with the analysis of such frequent samples and samples were taken every 200 miles for all subsequent tests. In order to determine wear by means of the Wear Index Test, such frequent samples are not strictly essential. It was felt, however, that frequent sampling would be advisable in order to obtain perfectly reliable data as regards ash and iron content. Samples were weighed, ignited, and ash content of the oil was determined. The resultant ash was

then fused with potassium hydrogen sulphate, dissolved in dilute sulphuric acid, and the iron content determined colorimetrically by ammonium thiocyanate. As a further check on the iron content, the iron was also determined volumetrically after reduction in a Jones reductor by titration with $\frac{N}{100}$ potassium permanganate.

Curves, as in Fig. 4, for iron and ash content against mileage during a test run show an initially high increase in ash and iron content, approaching a nearly constant value after the first 250 miles.

## Order of Tests.

The oils were tested in the engine in the following order :—

Test No. 1, Reference Oil.
Test No. 2, Synthetic Oil S/2.
Test No. 3, Synthetic Oil S/1.
Test No. 4, Reference Oil.

Tests Nos. 1–3 were carried out successfully without trouble. Test No 4 was run for 282 miles, when engine trouble developed and the test was shut down. On examining the engine, nothing was found to account for the rough running trouble which caused the shut down. The engine was reassembled and the test repeated. The engine ran smoothly for 490 miles, when rough running again occurred. The engine was again shut down and examined, when the white metal in No. 1 cylinder big-end bearing was found to be gone. The engine had up to now run for 20,000 miles at an equivalent road speed of 40 miles per hour. This trouble was undoubtedly purely mechanical, and had no connection with the lubricating oil, as exactly similar big-end trouble had already been experienced in the first 300 miles of the engine running in period, when the white metal in No. 1 cylinder big-end bearing was found to be gone. The trouble was rectified and the engine reassembled, and the repeat of test No. 4 on the reference oil carried out successfully.

## Results.

The wear, oil consumption, and cylinder deposit data are shown in Table I. The relative values, obtained as explained previously, should be

Table I.

*Actual and Relative Service Characteristics.*

| Property. | Run No. 1. | Run No. 2. | | | Run No. 3. | | | Run No. 4. |
|---|---|---|---|---|---|---|---|---|
| | Reference oil. | Oil S/2. | Interpolated reference oil. | Relative value. | Oil S/1. | Interpolated reference oil. | Relative value. | Reference oil. |
| Wear index, mgm. of iron/1000 miles | 3360 | 2300 | 2960 | 78 | 724 | 2600 | 28 | 1695 |
| Piston ring wear, mgm. of iron | 224·1 | 158·3 | 221·1 | 72 | 89·9 | 218·4 | 41 | 211·3 |
| Oil consumption, c.c./1000 miles | 2090 | 2300 | 2400 | 96 | 1680 | 2720 | 62 | 3520 |
| Deposits, gm./gall. oil used | 8·4 | 10·6 | 7·9 | 134 | 9·1 | 7·5 | 254 | 6·3 |

considered against a value of 100 for the reference oil. All relative values for a test oil below 100 indicate that the oil tested is superior to the reference oil. The properties of the oils before and after the 1500-miles engine test are given in Tables II and III.

TABLE II.

*Properties of Original Oils.*

| Oil. | Reference oil. | Synthetic oil, S/1. | Synthetic oil, S/2. |
|---|---|---|---|
| Specific gravity 60° F. . . . . | 0·926 | 0·908 | 0·929 |
| Viscosity at 100° F. (centistokes) . . | 212 | 430 | 273 |
| Viscosity at 200° F. (centistokes) . . | 17·9 | 38·8 | 25·1 |
| Viscosity index . . . . . | 70 | 110 | 100 |
| Viscosity gravity constant . . . | 0·865 | 0·825 | 0·864 |
| Conradson carbon per cent. . . . | 0·98 | 0·38 | 0·12 |
| Ramsbottom carbon, per cent. . . | 0·87 | 0·38 | 0·19 |

TABLE III.

*Properties of Oil after 1500 Miles Engine Test.*

| Oil. | Reference oil after Run No. 1. | Reference oil after Run No. 4. | Synthetic oil, S/1. | Synthetic oil, S/2. |
|---|---|---|---|---|
| Specific gravity 60° F. . . . | 0·929 | 0·925 | 0·918 | 0·938 |
| Viscosity at 100° F. (centistokes) | 219 | 185 | 492 | 353 |
| Total acidity (mgm. KOH per 1 gm. of oil) . . . . | 1·9 | 1·0 | 1·0 | 1·7 |
| Conradson carbon, per cent. . | 3·4 | 2·2 | 1·4 | 1·3 |
| Ramsbottom carbon, per cent. | 2·63 | 1·8 | 1·26 | 0·99 |
| Sludge, per cent. . . . . | 1·81 | 0·91 | 0·04 | 1·56 |
| Dilution, per cent. . . . . | 2·0 | 3·2 | 3·2 | 3·6 |

From the point of view of wear, the two synthetic oils were definitely superior to the proprietary brand reference oil, the synthetic oil obtained using an aluminium catalyst being also superior to that obtained using an aluminium chloride catalyst. The wear index and piston-ring wear data show fair agreement.

Both synthetic oils were superior to the reference oil on the basis of oil consumption, the oil prepared by the use of an aluminium catalyst being again superior to that prepared by the use of an aluminium chloride catalyst. This is interesting in view of the fact that the oil obtained using an aluminium catalyst S/1 is considerably more viscous than either the reference oil or the second synthetic oil S/2.

In the case of cylinder deposits, both synthetic oils are inferior to the reference oil. Once again, however, despite its higher viscosity synthetic oil, S/1 is superior to S/2.

The acidity, carbon residue increase, and viscosity increase of all the oils after use are very similar. The sludge content of the used oils in the case of the reference oil and the synthetic oil S/2 prepared with the aluminium chloride catalyst is also similar, but the synthetic oil S/1 prepared with the aluminium catalyst is superior in this respect.

## Conclusions.

The synthetic oils made by the condensation of chlorinated paraffin wax with benzene compare favourably with a proprietary brand market oil when subjected to bench tests in a four-cylinder water-cooled Morris 8 engine.

## Acknowledgment.

The authors have to thank Morris Motors for the loan of the Morris 8 engines used in this work.

### *References.*

[1] Langdon, *Monthly Bulletin, State College, Washington*, 1932, **15**, No. 2.
[2] Everett and Stewart, *Pennsylvania State College Bulletin*, No. 44.
[3] Boerlage and Gravensteyn, *Motorship*, 171, August 1932.
[4] Merrill, Moore, and Bray, *Refiner*, 1935, **14** (6), 313.

*Dept. of Oil Engineering and Refining,*
*The University,*
*Birmingham.*

# SIMPLE PETROLEUM TABLES FOR USE WITH DENSITY HYDROMETERS.*

By VERNEY STOTT, M.A., F.Inst.P.

ABSTRACT.

The paper gives two simple tables, (1) showing the change in density of petroleum oils with change in temperature, (2) for conversion of density in g./ml. to weight in air in lb. per Imperial gallon. Used in conjunction with a density hydrometer, the tables enable the weight of a known volume of oil, the volume of a known weight of oil, or the change in volume of a given quantity of oil with change in temperature to be obtained by very simple computations. Examples of the computations are given.

A note is appended on the accuracy of density determinations made by means of British Standard density hydrometers, and also notes explaining the derivation of the tables.

## TABLES REQUIRED.

THE object of this paper is to present two simple tables for use, in conjunction with a density hydrometer, for determining the weight of a known volume of oil or the volume of a known weight of oil.

Provided a density hydrometer with a suitably open scale is used—*e.g.*, a British Standard density hydrometer with sub-divisions equivalent to 0·0005 g./ml., a reading taken on the hydrometer in a liquid at any temperature may be taken as giving, to a sufficient degree of accuracy (see Note 1, p. 240), the density in g./ml. of the liquid at the temperature at which the hydrometer reading is taken.

Having thus obtained the density of the oil at any one temperature, its density at any other desired temperature may be obtained by means of Table I. This table gives values of $\beta \times 10^5$, $\beta$ being defined by the equation

$$\rho_t = \rho_{20} + \beta\,(20 - t) \qquad . \quad . \quad . \quad (1)$$

where $\rho_{20}$ is the density of the oil at 20° C. in g./ml.
and $\rho_t$ „ „ „ „ „ „ „ „ $t$° C. in g./ml.

The quantity $\beta$ is therefore the change in density of the oil in g./ml. per degree centigrade change in temperature.† It follows from equation (1) that if $\rho_{t_2}$ is the density of an oil at $t_2$ °C. and $\rho_{t_1}$ its density at $t_1$ °C. that

$$\rho_{t_2} = \rho_{t_1} + \beta(t_1 - t_2)$$

a relation which will be made use of later.

The values of $\beta$ given in Table I apply to petroleum oils having the densities $\rho_{20}$ given in the first column of the table. Only small second-order errors are introduced, however, by using for a liquid of known density $\rho_t$ the value of $\beta$ given for a value of $\rho_{20}$ in Table I numerically equal to $\rho_t$. For example, on this basis for $\rho_{40} = 0{\cdot}735$ g./ml. the value of $\beta$ is approximately

* Paper received 14th August, 1939.

† A table similar to Table I, but on a specific gravity basis, has already been published by E. S. L. Beale (*J. Instn. Petrol. Tech.*, 1937, **23**, 213).

0·00083, and this leads to an approximate value of $\rho_{20}$ equal to 0·735 + 20 × 0·00083—*i.e.*, 0·752 g./ml. The actual value of β corresponding to $\rho_{20}$ = 0·752 g./ml. is given in the Table as 0·00080, and this is a more accurate value to take for the liquid of density $\rho_{40}$ = 0·735 g./ml. The use of the approximate value 0·00083 instead of 0·00080 would, however, introduce an error of only 0·0006 g./ml. in the calculated density change over a temperature interval of 20° C. The more accurate value for β may always be obtained from Table I in the way that the value 0·00080 is obtained above. This refinement will, however, only be necessary when large temperature changes have to be allowed for and a high degree of accuracy is required, and when the determined value of $\rho_t$ is less than 0·86 g./ml.

The derivation of Table I is given in Note 2, p. 242.

TABLE I.

*Change in Density (β) in g./ml. per °C. of American Petroleum Oils.*

| $\rho_{20}$. | $\beta \times 10^5$. | $\rho_{20}$. | $\beta \times 10^5$. | $\rho_{20}$. | $\beta \times 10^5$. |
|---|---|---|---|---|---|
| 0·615 | 101 | 0·735 | 83 | 0·855 | 66 |
| 0·620 | 100 | 0·740 | 82 | 0·860 | 66 |
| 0·625 | 99 | 0·745 | 81 | 0·865 | 66 |
| 0·630 | 98 | 0·750 | 80 | 0·870 | 66 |
| 0·635 | 98 | 0·755 | 80 | 0·875 | 66 |
| 0·640 | 97 | 0·760 | 79 | 0·880 | 66 |
| 0·645 | 96 | 0·765 | 78 | 0·885 | 66 |
| 0·650 | 96 | 0·770 | 78 | 0·890 | 66 |
| 0·655 | 95 | 0·775 | 77 | 0·895 | 66 |
| 0·660 | 94 | 0·780 | 76 | 0·900 | 66 |
| 0·665 | 93 | 0·785 | 75 | 0·905 | 66 |
| 0·670 | 92 | 0·790 | 74 | 0·910 | 66 |
| 0·675 | 92 | 0·795 | 74 | 0·915 | 66 |
| 0·680 | 91 | 0·800 | 73 | 0·920 | 66 |
| 0·685 | 90 | 0·805 | 72 | 0·925 | 66 |
| 0·690 | 90 | 0·810 | 72 | 0·930 | 66 |
| 0·695 | 89 | 0·815 | 71 | 0·935 | 66 |
| 0·700 | 88 | 0·820 | 70 | 0·940 | 66 |
| 0·705 | 87 | 0·825 | 69 | 0·945 | 66 |
| 0·710 | 86 | 0·830 | 68 | 0·950 | 66 |
| 0·715 | 86 | 0·835 | 68 | 0·955 | 66 |
| 0·720 | 85 | 0·840 | 67 | 0·960 | 66 |
| 0·725 | 84 | 0·845 | 66 | 0·965 | 66 |
| 0·730 | 84 | 0·850 | 66 | | |

Having determined the density of the oil at any desired temperature *t* °C., Table II * serves to give the apparent weight in air in lb. of the quantity of the oil which occupies 1 gallon at *t* °C. The derivation of Table II is given in Note 3, p. 245.

* Table II was first published in the article "Hydrometers and Hydrometry," by V. Stott, *Report of the World Petroleum Congress*, Vol. II, p. 880, London, 1933, and has subsequently appeared in the British Standard Specification for Density Hydrometers No. 718—1936 and in "Standard Methods for Testing Tar and Its Products," 2nd edition, 1938.

TABLE II.

*Conversion of g./ml. to lb. per Imperial Gallon.*

| Density of oil in g./ml. at $t$ °C. | Correction for calculating the weight in lb. of the quantity of the oil which occupies 1 gallon at $t$ °C. |
|---|---|
| 0·60 | +0·000 2 |
| 0·65 | +0·000 3 |
| 0·70 | +0·000 4 |
| 0·75 | +0·000 6 |
| 0·80 | +0·000 7 |
| 0·85 | +0·000 8 |
| 0·90 | +0·000 9 |
| 0·95 | +0·001 0 |

*Note.*—The correction obtained from the second column is added to the density of the liquid at $t$ °C. and the sum multiplied by 10 to obtain the weight in lb. of the quantity of the oil which occupies 1 gallon at $t$ °C.

The use of Tables I and II in conjunction with readings taken on density hydrometers can best be illustrated by means of examples.

## EXAMPLES OF THE USE OF THE TABLES.

(1) *Determination of the Weight of a Known Volume of Oil.*

For this we require the weight of unit volume of the oil at the temperature at which the volume of the bulk of the oil is known. If the density of the oil is determined at this temperature, then Table I is not required, and the computation involves only the use of Table II as follows :—

*Example* (*a*).

Volume of oil at 29° C. . . . . 1056 gal.
Reading of B.S. density hydrometer in the oil at 29° C. . 0·8475 g./ml.

From Table II the weight of the quantity of the oil which occupies 1 gallon at 29° C. is

$$(0{\cdot}8475 + 0{\cdot}0008) \times 10 \text{ lb.}—i.e., 8{\cdot}483 \text{ lb.}$$

Hence the weight of the bulk of the oil is

$$(8{\cdot}483 \times 1056) \text{ lb.}—i.e., 8958 \text{ lb.}$$

Circumstances may require, however, that the density of the oil has to be determined at some temperature other than that at which the volume of the bulk of the oil is known. The use of Table I is then required as well as of Table II, but the computation is still a simple one as follows :—

*Example* (*b*).

Volume of oil at 29° C. . . . . 1056 gal.
Reading of B.S. density hydrometer in the oil at 15° C. . 0·8565 g./ml.

From Table I the value of $\beta \times 10^5$ of the oil is 66, so the density of the oil at 29° C. is [0·8565 — 0·00066 (29–15)] g./ml.—*i.e.*, 0·8473 g./ml. From

Table II the weight of the quantity of the oil which occupies 1 gal. at 29° C. is therefore

$$(0{\cdot}8473 + 0{\cdot}0008) \times 10 \text{ lb.}—i.e., 8{\cdot}481 \text{ lb.}$$

Hence the weight of the bulk of the oil is

$$(8{\cdot}481 \times 1056) \text{ lb.}—i.e., 8956 \text{ lb.}$$

In determining the weight of a known volume of oil it is clearly an advantage, when this is practicable, to determine the density of the oil at the temperature at which the volume of the bulk of the oil is known. No knowledge of the change in density of the oil with change in temperature is then necessary and Table I is not required.

(2) *Determination of the Volume of a Known Weight of Oil.*

For this we require the weight of unit volume of the oil at the temperature at which its volume is required. If the density of the liquid is determined at this temperature, then Table I is not required, and the computation involves only the use of Table II as follows :—

*Example* (*c*).

| | |
|---|---|
| Weight of oil . . . . . | 8958 lb. |
| Reading of B.S. density hydrometer in the oil at 20° C. | 0·8535 g./ml. |

If the volume of the oil at 20° C. is required then from Table II the weight of the quantity of the oil which occupies 1 gal. at 20° C. is (0·8535 + 0·0008) × 10 lb.—*i.e.*, 8·543 lb. The volume at 20° C. of the known weight of oil is therefore :—

$$(8958 \div 8{\cdot}543) \text{ gal.}—i.e., 1049 \text{ gal.}$$

If, however, circumstances have been such as to necessitate the hydrometer reading being taken at some temperature other than that at which the volume of the oil is required, then both Table I and Table II are required in the computations as follows :—

*Example* (*d*).

| | |
|---|---|
| Weight of oil . . . . . | 8958 lb. |
| Reading of B.S. density hydrometer in the oil at 20° C. | 0·8535 g./ml. |
| Temperature at which volume of oil is required . . | 60° F. |

From Table I the value of $\beta \times 10^5$ for the oil is 66, and so the density of the oil at 60° F. (15·$\dot{5}$° C.) is :—

$$[0{\cdot}8535 + 0{\cdot}00066\ (20–15{\cdot}\dot{5})] \text{ g./ml.}—i.e., 0{\cdot}8564 \text{ g./ml.}$$

From Table II the weight of the quantity of the oil which occupies 1 gal. at 60° C. is therefore :—

$$(0{\cdot}8564 + 0{\cdot}0008) \times 10 \text{ lb.}—i.e., 8{\cdot}572 \text{ lb.}$$

The volume at 60° F. of the known weight of oil is hence :—

$$(8958 \div 8{\cdot}572) \text{ gal.}—i.e., 1045 \text{ gal.}$$

In determining the volume of a known weight of oil it is clearly an advantage, when this is practicable, to determine the density of the oil at the temperature at which its volume is required. No knowledge of the change in density of the oil with change in temperature is then necessary, and Table I is not required.

(3) *Determination of the Volume at any Desired Temperature of a quantity of Oil having a Known Volume at a Known Temperature.*

Since the volume of any given mass of oil is inversely proportional to its density, Table I serves to determine the change in volume resulting from a change in the temperature of a quantity of oil of known volume at the original temperature, provided that the density of the oil $\rho_t$ at any temperature $t$ °C. is known. The following examples illustrate the computations :—

*Example* (*e*).

| | |
|---|---|
| Volume of oil at 29° C. . . . . | 1056 gal. |
| Reading of B.S. density hydrometer in the oil at 29° C. | 0·8475 g./ml. |
| Temperature at which the volume of the oil is required | 20° C. |

From Table I the density of the oil at 20° C. is :—

$$[0{\cdot}8475 + 0{\cdot}00066\ (29–20)]\ \text{g./ml.}—i.e.,\ 0{\cdot}8534\ \text{g./ml.}$$

The volume of the oil at 20° C. is equal to :—

$$\text{Volume of oil at 29° C.} \times \frac{\text{Density of oil at 29° C.}}{\text{Density of oil at 20° C.}}$$

*i.e.*, to $(1056 \times 0{\cdot}8475 \div 0{\cdot}8534)$ gal. = 1049 gal.

*Example* (*f*).

| | |
|---|---|
| Volume of oil at 29° C. . . . . | 1056 gal. |
| Reading of B.S. density hydrometer in the oil at 20° C. . | 0·8535 g./ml. |
| Temperature at which the volume of the oil is required | 60° F. |

From Table I the value of $\beta \times 10^5$ for the oil is 66, and hence the density of the oil at 29° C. is :—

$$[0{\cdot}8535 + 0{\cdot}00066\ (20–29)]\ \text{g./il.}—i.e.,\ 0{\cdot}8476\ \text{g./ml.}$$

and at 60° F. (15·5̇° C.) :—

$$[0{\cdot}8535 + 0{\cdot}00066\ (20–15{\cdot}5\dot{})]\ \text{g./ml.}—i.e.,\ 0{\cdot}8564\ \text{g./ml.}$$

The volume of the oil at 60° F. is equal to :—

$$\text{Volume of oil at 29° C.} \times \frac{\text{Density of oil at 29° C.}}{\text{Density of oil at 60° F.}}$$

*i.e.*, to $(1056 \times 0{\cdot}8476 \div 0{\cdot}8564)$ gal. = 1045 gal.

It will be seen from a comparison of examples (*e*) and (*f*) that the computation is simpler if the hydrometer reading is taken either at the temperature at which the volume of the oil is known or at the temperature at which the volume of the oil is required.

## Notes.

(1) *Accuracy of Density Determination by Means of B.S. Density Hydrometers.*

In the foregoing examples the directly observed reading on a British Standard density hydrometer, adjusted to indicate density in g./ml. at 20° C., has been taken as giving directly the density of the oil in g./ml. at the temperature at which the hydrometer reading was taken. It is desirable to estimate the errors resulting from this.

It will be assumed that a B.S. density hydrometer, having a scale subdivided into intervals of 0·0005 g./ml., is used and that, in order to make the minimum demand on the operator, he is instructed to record the reading as that corresponding to the graduation mark nearest to the level liquid surface, thus relieving the operator of the necessity of estimating fractions of a subdivision. The corrections to be applied to the observed reading to obtain the density of the oil at the temperature at which the hydrometer reading is taken are those for :—

(*a*) the scale error of the hydrometer,
(*b*) the change in volume of the hydrometer between its standard temperature 20° C. and the temperature at which it is read in the oil,
(*c*) the difference between the surface tension of the oil and that for which the B.S. hydrometer is adjusted.

From Table 3, p. 12, of B.S. 718 * the maximum correction under (*a*) would be ± 0·0004 g./ml.

As regards (*b*) we will assume that the hydrometer is read at a temperature differing by 20° C. from the standard temperature of the hydrometer—*i.e.*, either at 0° C. or 40° C.—and that the observed hydrometer reading is 0·845 g./ml. From Table 6, p. 29, of B.S. 718 the correction under (*b*) would be +0·0004 g./ml. at 0° C., and − 0·0004 g./ml. at 40° C. The B.S. density hydrometers covering the density range 0·650 g./ml. to 1·000 g./ml. are adjusted for surface tensions very close to those of petroleum oils so that the correction under (*c*) is negligible.

Collecting all these corrections together, and assuming also that the actual hydrometer reading was midway between two graduation marks on the hydrometer scale, so that the recorded reading is in error by ± 0·00025 g./ml. (*d* say) due to rounding off to the reading to the nearest graduation mark, we have :—

| | | |
|---|---|---|
| Correction | (*a*) | ±0·0004 g./ml. |
| ,, | (*b*) | ±0·0004 g./ml. |
| ,, | (*c*) | 0·0000 g./ml. |
| ,, | (*d*) | ±0·00025 g./ml. |
| Total possible range of corrections | | ±0·00105 g./ml. |

* *I.e.*, "British Standard Specification for Density Hydrometers," No. 718—1936.

In an extreme case therefore where

(*a*) the hydrometer was assumed to have the maximum error permissible under the B.S. specification;

(*b*) a generous allowance of 20° C. was made for the difference between the standard temperature of the hydrometer and the temperature at which the hydrometer was read;

(*c*) the liquid surface was assumed to be midway between two graduation marks, and the reading recorded as one or other of these graduation marks,

the total error is only one unit in the third place of decimals when the directly observed hydrometer reading is taken as giving directly the density of the oil at the temperature of observation. In general, the error would be less than in the extreme case considered.

The error can be substantially reduced, if necessary, by using a hydrometer furnished with a certificate of corrections by The National Physical Laboratory and applying appropriate corrections in accordance with the tables given in B.S. 718. The possible range of the uncertainty in the final result would then be :—

| | |
|---|---|
| (*a*) Maximum error in certified correction . | ± 0·0002 g./ml.* |
| (*b*) Error due to corrections in Table 6 of B.S. 718 rounded off to the nearest 0·0001 g./ml. | ± 0·00005 g./ml. |
| (*c*) Negligible surface tension correction . . | 0·0000 g./ml. |
| (*d*) Assuming one-tenth of a subdivision error in estimating scale reading . . . | ± 0·00005 g./ml. |
| Total possible uncertainty in density | ± 0·0003 g./ml. |

The value ± 0·0003 g./ml. thus derived is again a maximum estimate of the possible error, and in general the actual error would be smaller.

Whether the extra trouble of applying corrections to the hydrometer readings is necessary is a matter for decision by the user on the basis of the accuracy aimed at in his gauging operations. The hydrometer used, however, should be one known at least not to have errors in excess of the B.S. tolerances.

The errors associated directly with the hydrometer have alone been considered, but of course any error in determining the temperature of the oil at the time of taking the hydrometer reading would be reflected as an error in the density of the oil. From Table I the error resulting from 0·1° C. error in temperature would be 0·0001 g./ml. for densities in the neighbourhood of 0·7 g./ml. and 0·00007 g./ml. for densities of 0·8 g./ml. and upwards with intermediate values for intermediate densities.

* The corrections actually determined in the N.P.L. tests of the hydrometers in question are rounded off to the nearest 0·0002 g./ml. on the certificates issued, so that in extreme cases an error of ±0·0001 g./ml. might result from rounding off. Allowing another ±0·0001 g./ml. for possible error in the actually determined correction the total possible error ±0·0002 g./ml. quoted above is arrived at. This is clearly a maximum estimate which would only arise in extreme cases.

(2) *Derivation of Table I.*

Table I has been derived from Tables 7, 8, and 9 of "Density and Thermal Expansion of American Petroleum," by H. W. Bearce and E. L. Peffer, Technologic Paper No. 77 of the National Bureau of Standards, 1916. It is stated in "National Standard Petroleum Oil Tables," Circular No. C. 410, of the National Bureau of Standards, issued 1936, that these tables are largely based on the Technologic Paper No. 77.

Table 7 of the Technologic Paper No. 77 gives densities at various temperatures over the range 0–50° C., generally at each 10° C., of fifty-four refined oils of densities at 20° C. ranging from 0·618 g./ml. to 0·942 g./ml.

Table 8 gives densities of twelve crude oils at 0° C., 25° C., and 50° C., of one at 0° C. and 25° C. and of five at 30° C. and 40° C., the range of densities at 20° C. being 0·811 g./ml. to 0·963 g./ml.

Table 9 gives densities of fifteen fuel oils and lubricating oils at 25° C., 50° C., 75° C., and 90° C., the range of densities at 20° C. being 0·865 g./ml. to 0·957 g./ml.

First of all it was assumed that the densities given could be represented by

$$\rho_t = \rho_{20} + \beta(20 - t)$$

and values of $\rho_{20}$ and $\beta$ were calculated for each of the eighty-seven oils, the method of least squares being used when more than two densities were available for any given oil. From the resulting values of $\beta$ and $\rho_{20}$ values of $\rho_t$ were calculated for each of the oils for each temperature at which the density of the oil was given in the original tables. Values of $\beta$ taken to only two significant figures were used in the calculation of $\rho_t$, as not more than two significant figures would normally be employed. The differences between the calculated values of $\rho_t$ and the values given in the original tables were noted. An analysis of these differences for the refined oils is given in Table A.

TABLE A.

*Differences between Calculated Values of $\rho_t$ and Tabulated Densities for Refined Oils.**

| Maximum difference between calculated and given density for any given oil. | Number of oils having maximum difference given in preceding column. | Maximum difference between calculated and given density for any given oil. | Number of oils having maximum difference given in preceding column. |
|---|---|---|---|
| 0·0000 g./ml. | 2 | 0·0006 g./ml. | 1 |
| 0·0001 ,, | 28 | 0·0007 ,, | 1 |
| 0·0002 ,, | 10 | 0·0008 ,, | 0 |
| 0·0003 ,, | 4 | 0·0009 ,, | 0 |
| 0·0004 ,, | 1 | 0·0010 ,, | 1 |
| 0·0005 ,, | 1 | 0·0011 ,, | 1 |

* The numbers in the second columns of Table A make a total of 50, as against a total of 54 oils for which data are given in Table 7. This is because residuals have not been included for four of the oils for which only two values of the density were given as for these the residuals would necessarily be zero.

From Table A it will be seen that the calculated densities of the refined

oils agreed closely for nearly all the oils * with the given densities, *i.e.*, the relation

$$\rho_t = \rho_{20} + \beta(20 - t)$$

satisfactorily represents the change in density of the oils with change in temperature, over the range 0–50° C. for which densities were available.

An analysis of the residuals for the twelve crude oils for which densities were given at the three temperatures 0° C., 25° C., and 50° C. is given in Table B.

TABLE B.

*Differences between Calculated Values of $\rho_t$ and Tabulated Densities for Twelve Crude Oils.*

| Maximum difference between calculated and given density for any given oil. | Number of oils having maximum difference given in preceding column. |
|---|---|
| 0·0000 g./ml. | 0 |
| 0·0001 ,, | 3 |
| 0·0002 ,, | 3 |
| 0·0003 ,, | 0 |
| 0·0004 ,, | 3 |
| 0·0005 ,, | 2 |
| 0·0005 ,, | 1 |

The residuals are rather larger than for refined oils, but still not excessive.

An analysis of the residuals for the fifteen fuel oils and lubricating oils for which densities were given at 25° C., 50° C., 75° C., and 90° C. is given in Table C.

TABLE C.

*Differences between Calculated Values of $\rho_t$ and Tabulated Densities for Fifteen Fuel Oils and Lubricating Oils.*

| Maximum difference between calculated and given density for any given oil. | Number of oils having maximum difference given in preceding column. |
|---|---|
| 0·0000 g./ml. | 0 |
| 0·0001 ,, | 2 |
| 0·0002 ,, | 5 |
| 0·0003 ,, | 5 |
| 0·0004 ,, | 0 |
| 0·0005 ,, | 0 |
| 0·0006 ,, | 2 |
| 0·0007 ,, | 1 |

Here four-fifths of the maximum differences between the calculated and tabulated densities do not exceed 0·0003 g./ml., although the temperature range covered was 25–95° C.

* Three of the four oils exhibiting differences greater than 0·0005 in Table A were stated in the original paper probably to contain solid particles at the lower temperatures.

Tables A to C having established that, for the large majority of the oils, the calculated values of $\rho_{20}$ and $\beta$ could be used to calculate to a high degree of accuracy the density of the oils at any required temperature, within the temperature range of the given data, by means of the relation :—

$$\rho_t = \rho_{20} + \beta(20 - t)$$

corresponding values of $\beta$ and $\rho_{20}$ were plotted on a graph. From inspection of this graph it was evident that for all values of $\rho_{20}$ from 0·845 g./ml. to 0·965 g./ml. a mean value 66 could be taken as a reasonable value for $\beta \times 10^5$. For densities below 0·845 g./ml. the values of $\beta$ were evenly distributed about an inclined straight line, and the equation of this line was found, by the method of least squares, to be :—

$$\beta = (193{\cdot}02 - 150{\cdot}03\ \rho_{20}) \times 10^{-5}$$

The values of $\beta$ given in the earlier part of Table I were calculated from this relation, and the mean value 66 for $\beta \times 10^5$ for higher values of $\rho_{20}$ was used for Table I.

The value of $\beta$ ($\beta_s$, say) derived from the above equation, or taken as $66 \times 10^{-5}$ according to the value of $\rho_{20}$, was calculated from the density $\rho_{20}$ of each of the eighty-seven oils. The difference $\beta - \beta_s$ was noted for each oil, this difference being that between the value of $\beta$ derived directly from the given densities of the oil and the value of $\beta$ ($\beta_s$) obtained from the general relationship between $\rho_{20}$ and $\beta$ forming the basis of Table I. An analysis of these differences is given in Table D.

TABLE D.

*Differences between Values of $\beta$ Calculated from Density of Oil at 20° C. and Values of $\beta$ Calculated from a Series of Experimentally Determined Densities at Different Temperatures.*

| Magnitude of $(\beta_s - \beta) \times 10^5$, $\beta$ calculated from $\rho_{20}$, $\beta$ calculated from series of densities. | Number of differences of magnitudes given in first column— | | |
|---|---|---|---|
| | Refined oils. | Crude oils, fuel oils and heavy lubricating oils. | Total. |
| Less than −5 | 0 | 0 | 0 |
| −5 | 0 | 0 | 0 |
| −4 | 1 | 1 | 2 |
| −3 | 1 | 3 | 4 |
| −2 | 15 | 7 | 22 |
| −1 | 7 | 2 | 9 |
| 0 | 12 | 5 | 17 |
| +1 | 5 | 4 | 9 |
| +2 | 4 | 4 | 8 |
| +3 | 5 | 2 | 7 |
| +4 | 0 | 2 | 2 |
| +5 | 1 | 2 | 3 |
| Greater than +5 | 3 | 1 | 4 |

For only four out of the eighty-seven oils was the difference $(\beta_s - \beta) \times 10^5$ greater than 5, and three of these were stated in the original paper to be oils which probably contained solid particles at lower temperatures. The difference in the changes in density for 20° C. change in temperature calculated from values of $\beta$ differing by 0·00005 is 0·001 g./ml. Hence close agreement in calculated changes of density would be obtained between changes calculated on the basis of the value of $\beta$ for the individual oil and changes calculated from values of $\beta$ obtained from Table I. This is further illustrated by the fact that for sixty-six out of the eighty-seven oils $(\beta_s - \beta) \times 10^5$ did not exceed 2, corresponding to a difference of only 0·0004 g./ml. in the density change for 20° C. change in temperature according to whether $\beta_s$ or $\beta$ is used in the calculations.

The values of $\beta_s$ given in Table I may therefore safely be used for petroleum oils of the type investigated in the National Bureau of Standards Technologic Paper No. 77.*

(3) *Derivation of Table II.*

Let $\rho_t$ = density—mass per unit volume—of oil in g./ml. at $t$ °C.
„ $W$ = observed weight in air in lb. of a quantity of the oil which occupies 1 gal. at $t$ °C.

The equation for the equilibrium at the time of weighing is :—

$$W \times G\left(1 - \frac{\sigma}{\Delta}\right) = K(\rho_t - \sigma) \quad . \quad . \quad . \quad (1)$$

where $G$ = number of grams in 1 lb.—*i.e.*, 453·592.
$\sigma$ = density of air at time of weighing—assumed to be 0·0012 g./ml.
$\Delta$ = density of weights used, assumed to be 8·3 g./ml.
$K$ = number of millilitres in a gallon—*i.e.*, 4545·96.

From (1) we have :—

$$W = \frac{K}{G} \times \frac{1}{(1 - \sigma/\Delta)} \times (\rho_t - \sigma) \quad . \quad . \quad . \quad (2)$$

The coefficient of $(\rho_t - \sigma)$ in (2) is constant and the equation is in a convenient form for computing values of $W$ for different values of $\rho_t$.

Finally let $c$ be the correction given in Table II.

Then $$W = 10(\rho_t + c)$$

or $$c = \frac{W}{10} - \rho_t \quad . \quad . \quad . \quad . \quad (3)$$

and in the construction of Table II values of $c$ were computed by means of (3) from values of $W$ derived from (2).

*The National Physical Laboratory,*
*Teddington, Middlesex.*

* The values of $\beta$ in Table I agree on the average to within 0·00002 with the "Specific Gravity Correction Factors per ° F." table given by E. S. L. Beale, *J. Instn Petrol Tech.*, 1937, **23**, 213, when the latter are converted to the same basis. Close agreement was to be expected, since both tables were derived from the same original data. Beale's values were derived from the N.B.S. Circular No. 154 by a rather less rigid method than that employed in the present paper in obtaining values of $\beta$ directly from Technologic Paper No. 77, on which Circular No. 154 was based.

# PHYSICAL CONSTANTS OF ASPHALTIC BITUMENS.

## PART II.*

By Dr. R. N. J. Saal, K. Meinema, and Dr. P. C. Blokker.

Summary.

This paper gives a survey of the following electrical properties of asphaltic bitumens :

dielectric strength,
angle of dielectric loss,
dielectric constant,
electrical conductivity.

The methods by which these properties have been determined are described in detail.

### Introduction.

A survey is given of some electrical properties of asphaltic bitumens in continuation of a publication from the Laboratory of the N.V. De Bataafsche Petroleum Maatschappij describing various other physical constants of these substances.[1]

The dielectric strength, dielectric loss, and dielectric constant of asphaltic bitumen are of great importance for the different applications of bitumen in the electrical industry, where it is used, for instance, in pothead compounds, sealing compounds for transformers, impregnation material for condensers, insulation material for cables, etc.

### A. Dielectric Strength.

The dielectric strength of a material is the minimum value of the electric-field intensity at which a disruptive discharge occurs in the material under specified conditions.

The dielectric strength is determined with an apparatus in which the material under test is placed between two electrodes. The result of the test is largely governed by the shape of the electrodes and the distance between them.

Usually, an apparatus with two plate or two spherical electrodes is used.

The plate electrodes have a considerable advantage over spherical electrodes, in that any contamination of the bitumen is more easily discovered. In agreement with this, the dielectric strength found with spherical electrodes is invariably higher than that measured with plate electrodes.

In the case of bitumens, the use of plate electrodes has the further advantage that the prevailing conditions more closely simulate actual practice.

For these reasons, part of the measurements were carried out by means of an apparatus with plate electrodes, developed by G. W. Nederbragt.[2] Moreover, measurements were made with spherical electrodes in accordance with the British Standard Specification Test No. 688—1936.[3]

* Paper received 18th January, 1940.

### Plate Electrodes.

Fig. 1 is a sketch of the apparatus with plate electrodes. In this apparatus the dielectric strength is measured between two flat, disk-shaped electrodes, *A* and *B* (diameter 40 mm.), with rounded edges. The electrode *A* is supported by the rectangularly bent rod *C*, which has been cemented into the porcelain tube. All the metal parts of the apparatus are made of nickel steel with a low coefficient of expansion (Invar).

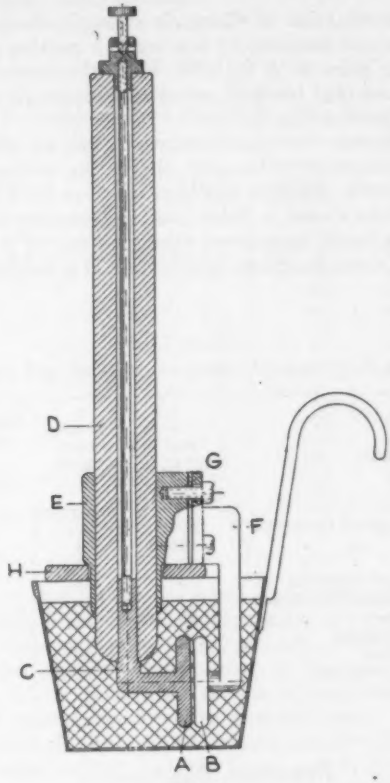


Fig. 1.

APPARATUS FOR DETERMINATION OF DIELECTRIC STRENGTH OF SEALING COMPOUNDS.

To the porcelain tube the block *E* has been soldered, so that one side of the block is in the same vertical plane as electrode *A*. The electrode *B* is connected to block *E* by means of the rod *F*, and the plate *G* being in one vertical plane with electrode *B*. The desired distance between *A* and *B* may be adjusted by inserting a small plate between *E* and *G*.

The principal advantage of the use of Invar is that it can be cemented

into porcelain without fear of the porcelain cracking when it is heated up to 200° C.; an additional advantage is that the position of the electrode *A* with respect to the porcelain tube always remains the same, owing to the low coefficient of expansion of Invar.

In various experiments it was, indeed, found that the distance between the electrodes *A* and *B* changes but very little with the temperature. The 1 mm. distance between the two electrodes may be previously checked by means of a template (thickness of thin end 0·98 mm., thick end 1·02 mm.).

Before the determination of dielectric strength the asphaltic bitumen was freed from air and moisture by heating in a melting pan to 80–100° C. above its softening point R. & B., after which the electrodes were lowered into the bitumen, so that block *E* rested on support *H*, which was placed over the melting pan (cf. Fig. 1).

In these experiments we usually started from an effective tension of 15 kilovolts; the tension (a 50-cycle alternating voltage) was increased stepwise by 5 kilovolts effective, and kept constant for 1 minute after each increase. The values stated in Table I are the tensions which the material could withstand without breakdown taking place. The figures are mean values from three determinations, which showed a maximum difference of 5 kilovolts.

TABLE I.

*Dielectric Strength of Asphaltic Bitumens Measured with Plate Electrode.*

| Bitumen. | Pen./ 25° C. | Softening point, R. & B., ° C. | Dielectric strength in effective Kv./mm. | |
|---|---|---|---|---|
| | | | 20° C. | 50° C. |
| Venezuelan steam reduced bitumen. | 180 | 39½ | 10 | <10 |
| Ditto . . . . . | 43½ | 54 | 30 | 10 |
| Ditto . . . . . | 23 | 61 | 30 | 10 |
| Mexican steam reduced bitumen . | 25 | 63 | 35 | 10 |
| Venezuelan steam reduced bitumen. | 11 | 83 | >60 | 15 |
| Mexican blown bitumen . . | 35 | 88½ | 30 | 20 |
| Venezuelan blown bitumen . . | 39 | 86½ | 25 | 15 |
| Mexican blown bitumen . . | 11 | 129 | 35 | 15 |
| Bitumen from cracked residue . | 1½ | 74 | >60 | 20 |
| Light-coloured bitumen . . | 15 | 55 | 30 | 14 |

## SPHERICAL ELECTRODES.*

The dielectric strength measurements with spherical electrodes were carried out in accordance with the British Standard Specification Test No. 688—1936.[3]

The spherical electrodes, 0·5 inch (approximately 13 mm.) diameter, were arranged horizontally 0·05 inch apart in a porcelain container, into which the bitumen was poured.

* The determinations referred to were carried out at the Central Laboratories of the Shell Marketing Co., Ltd., London, to whom we are indebted for the permission to publish these data.

Before the determination the asphaltic bitumen was freed from air and moisture by heating to 75–90° C. (dependent on the softening point) above the softening point of the bitumen. After cooling down slowly to test temperature the bitumen was maintained thereat for 1 hour before the measurement was made. In the experiments the voltage (a 50-cycle alternating voltage) was raised gradually from zero to the appropriate voltage (10,000 or 20,000 volts) in approximately 10 seconds, and was maintained at this voltage for 1 minute. The voltage was then raised until the breakdown voltage was obtained.

The results found are given in Table II.

TABLE II.

*Dielectric Strength of Asphaltic Bitumen Measured with Spherical Electrodes (according to British Standard Specification Test No. 688—1936).*

| Bitumen. | Pen./ 25° C. | Softening point, R. & B., ° C. | Dielectric strength in effective Kv./mm. 60° C. |
|---|---|---|---|
| Venezuelan steam-reduced bitumen | abt. 450 | abt. 32 | 28 41 |
| | ,, 300 | ,, 35 | 11 12 13 27 |
| | ,, 210 | ,, 38 | 17 33 33 35 36 |
| | ,, 100 | ,, 45 | 40 |
| | ,, 90 | ,, 46[5] | 24 45 |
| | ,, 65 | ,, 50 | 27 38 40 45 45 |
| | ,, 45 | ,, 55 | 35 39 40 43 |
| | ,, 35 | ,, 57[5] | 36 36 38 |
| | ,, 25 | ,, 61[5] | 22 37 38 |
| | ,, 15 | ,, 71 | 27 35 41 |
| | ,, 9 | ,, 85 | 22 |
| | ,, 4 | ,, 115 | (>40 at 90° C.) |
| Venezuelan blown bitumen | ,, 40 | ,, 85 | 35 |
| | ,, 25 | ,, 85 | 30 |
| Bitumen from cracked residue Trinidad Epuré | ,, 1½ | ,, 72 | 36 (15 at 90° C.) |

Each figure is a mean value of three measurements. The different values given for each bitumen grade in increasing order of magnitude refer to samples from different charges and from different refineries.

It will be noticed that different samples of one grade sometimes give widely divergent values. This may be due to variations in the amount of mineral matter present, such as salt, iron scale, etc. The same phenomenon has been observed, although to a smaller extent, with plate electrodes. The explanation may be that with the larger active surface of the plate electrodes there is a greater possiblity of contamination occurring between the electrodes, owing to which there is less variation in results.

Tables I and II show that spherical electrodes usually give far higher figures for dielectric strength than plate electrodes. This may be due to the same fact.

## B. DIELECTRIC LOSSES.

When an insulating material is exposed to an alternating electric field, so-called dielectric losses usually occur, which manifest themselves as heat evolution. These losses play an important part in insulation technique,

for instance, when a current is sent through a cable; this involves loss of electrical energy, while, moreover, the condition of the cable may be adversely affected by the generated heat.

These losses are partly due to *dielectric hysteresis* and partly to *Ohmic conduction*.

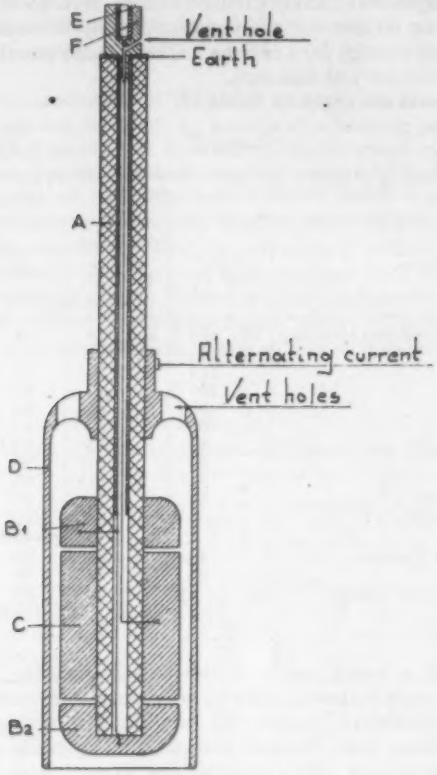


FIG. 2.

APPARATUS FOR DETERMINATION OF DIELECTRIC LOSSES, DIELECTRIC CONSTANTS AND CONDUCTIVITY OF ASPHALTIC BITUMENS.

In the case of a given material and at a definite temperature, both kinds of loss are proportional to the square of the effective voltage. Moreover, the losses caused by dielectric hysteresis increase strongly with the frequency of the alternating current.

As a measure of the losses brought about by *dielectric hysteresis* we used the tangent of the angle of dielectric loss. By the angle of dielectric loss we understand here the phase difference between the dielectric loss current and the dielectric displacement current (*i.e.*, the "wattless" current that would flow if the material were an ideal dielectric).

As a measure of the *loss due to conduction* we used the specific conductance.

The determination of the angle of dielectric loss and the dielectric constant was carried out at a 50-cycle alternating voltage, using a Schering bridge and a cylindrical condenser, which was filled with the bitumen under examination.

A sketch of the cylindrical condenser is given in Fig. 2. The inner cylinder $C$, made of polished Poldi metal, is cemented on to the porcelain tube $A$, and connected to the zero indicator (vibration galvanometer) of the Schering bridge by means of the head-piece $E$ (which is insulated from the earth by the fibre tube $F$). The potential difference between the inner cylinder $C$ and the earth is very slight (about 0·1 volt). The outer cylinder $D$ (also made of polished Poldi metal) is screwed on to a ring which is cemented into the porcelain tube, and which is connected to a supply transformer. Further, there are two guard rings, $B^1$ and $B^2$, which are earthed via the conducting inner wall of the porcelain tube, and which serve to maintain the most homogeneous field possible between the cylinders $C$ and $D$, and to prevent leakage currents from occurring along the porcelain tube.

This apparatus was placed in liquid bitumen; the air could escape through the vent holes. Next, the apparatus was cooled to the desired temperature.

In the experiments the electrical field intensity between the cylinders $C$ and $D$, which were 3 mm. apart, was about 20 kilovolt effective per cm.

These measurements yielded:

1. The angle of loss, the tangent of which indicates the relation between power-consuming current (dielectric loss current + conduction current) and the "wattless" electric displacement current;
2. The capacity of the condenser filled with bitumen (about 100 cm.). Since the capacity of the air-filled condenser is measured as well, the *dielectric constant* is found as the quotient of these two capacities.

The angle of loss thus found is not a direct measure of the losses caused by hysteresis, as the angle measured is also affected by ohmic conduction.

As that part of the angle of loss which is caused by ohmic conduction depends on the frequency in quite a different way from the part due to hysteresis, it is desirable to separate the two parts. The separation takes place so that the losses due to hysteresis are expressed by an angle (angle of dielectric loss), the ohmic losses being expressed by the specific conductance. It was necessary, therefore, to determine also the latter magnitude (this determination is described further on).

The separation was made according to the following equations:

$$\text{loss due to hysteresis} = \frac{2\pi}{9\times10^{11}} f E^2_{ett.} C \tan \delta_H \quad . \quad . \quad (1)^*$$

$$\text{loss due to conduction} = \frac{E^2_{ett.}}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* The factor $9\times10^{11}$ is used because the capacity, unlike the other magnitudes, is not expressed in technical units, but in electrostatic units. The technical unit of capacity (farad) = $9\times10^{11}$ the electrostatic unit (cm.).

where $f$ = frequency.
$E_{eff.}$ = effective potential in volts.
$C$ = capacity in cm of the bitumen-filled condenser.
$\delta_H$ = angle of loss caused by hysteresis.
$R$ = resistance in ohms.

The ohmic losses may also be expressed by an angle. If dielectric hysteresis is absent, the following equation holds :

$$\tan \delta_0 = \frac{\text{conduction current}}{\text{displacement current}} = \frac{\frac{E_{eff.}}{R} 9 \times 10^{11}}{E_{eff.} 2\pi f C} = \frac{9 \times 10^{11}}{R 2\pi f C} . \quad (3)$$

where $\delta_0$ = angle of loss caused by ohmic conduction.

From (2) and (3) it follows that :

$$\text{Loss due to conduction} = \frac{2\pi}{9 \times 10^{11}} f E^2_{eff.} C \tan \delta_0 . \quad . \quad (4)$$

As the angle of loss is in general small, this equation also holds, approximately, when hysteresis takes place; therefore :

$$\tan \delta_{tot.} = \text{approx. } \tan \delta_H + \tan \delta_0.$$

In accordance with equations (1) and (4), the total loss is therefore :

$$= \frac{2\pi}{9 \times 10^{11}} f E^2_{eff.} C \tan \delta_{tot.} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$\delta_{tot.}$, the total angle of loss, is the angle found in our measurements. If the resistance is determined at the same time, $\tan \delta_0$ is also known (from (3)), and $\tan \delta_H$ may be calculated as follows :

$$\tan \delta_H = \tan \delta_{tot.} - \tan \delta_0$$
$$= \tan \delta_{tot.} - \frac{9 \times 10^{11}}{R 2\pi f C}$$

As the specific conductance $= \frac{1}{4\pi C_0 R}$ ($C$ = capacity of the air-filled condenser, and $C = C_0 \epsilon$; $\epsilon$ = dielectric constant), it follows that :

$$\tan \delta_H = \tan \delta_{tot.} - \frac{18 \times 10^{11} \lambda}{f \epsilon} . \quad . \quad . \quad . \quad . \quad (6)$$

($\lambda$ = specific conductance.)

For purpose of illustration we append an example of the calculation of the tan $\delta_H$ of a Venezuelan distilled bitumen at 90° C. (No. 3 of Table III).

Measured : $\tan \delta_{tot.} = 0{\cdot}025$.
$\lambda = 5{\cdot}8\ 10^{-13} \Omega^{-1}$ cm.$^{-1}$
$f = 50$
$\epsilon = 2{\cdot}88$.

Thus, in accordance with equation (6) :

$$\tan \delta_H = 0{\cdot}025 - 0{\cdot}007 = 0{\cdot}018.$$

TABLE III.

*Angle of Loss, Dielectric Constant and Specific Conductance of Asphaltic Bitumens at Different Temperatures.*

TABLE III.

*Angle of Loss, Dielectric Constant and Specific Conductance of Asphaltic Bitumens at Different Temperatures.*

| Asphaltic bitumen. | Temp., ° C. | Steam reduced, Venezuelan bitumen. | | | Steam reduced Mexican bitumen. | | Blown Mexican bitumen. | | | Bitumens from cracked residues. | | Light-coloured bitumen. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | 11. |
| Penetration at 25° C. (SAM 68/38) | — | 175 | 23 | 11 | 25 | 19½ | 38 | 22½ | 11 | 19 | 1½ | 15 |
| Softening point, R. & B. (SAM 67/38), ° C. | — | 39½ | 64 | 86 | 65 | 67½ | 80 | 77 | 129 | 58 | 74 | 55 |
| *Tangent of the total angle of loss × 100 (loss due to hysteresis + loss due to ohmic conduction) | 5 | 2·0 | 1·4 | 0·7 | 1·2 | 1·4 | 1·7 | 1·7 | — | 1·2 | — | 0·2 |
| | 20 | 2·1 | 1·9 | 1·4 | 1·8 | 2·0 | 1·3 | 1·9 | 1·4 | 2·3 | 1·0 | 1·5 |
| | 35 | 2·0 | 2·0 | 1·8 | 1·8 | 2·3 | 1·2 | 1·8 | 1·4 | 2·6 | 1·8 | 3·3 |
| | 50 | 2·9 | 1·9 | 1·7 | 1·7 | 2·3 | 1·5 | 1·7 | 1·3 | 2·2 | 2·1 | 2·5 |
| | 65 | ca. 9·0 | 2·1 | 1·5 | 2·2 | 2·4 | 2·3 | 1·9 | — | 2·9 | — | 1·0 |
| | 80 | — | 3·7 | 1·7 | 4·6 | 4·1 | 5·1 | 2·9 | — | 9·9 | — | 2·4 |
| | 90 | — | 7·8 | 2·5 | — | 7·2 | 8·3 | 4·5 | — | — | — | 5·6 |
| | 100 | — | — | 4·3 | — | — | — | — | — | — | — | — |
| Tangent of the angle of loss due to hysteresis × 100 (only for losses caused by dielectric hysteresis) | 5 | 2·0 | 1·4 | 0·7 | 1·2 | 1·4 | 1·7 | 1·7 | — | 1·2 | — | 0·2 |
| | 20 | 2·1 | 1·9 | 1·4 | 1·8 | 2·0 | 1·3 | 1·9 | 1·4 | 2·3 | 1·0 | 1·5 |
| | 35 | 1·9 | 2·0 | 1·8 | 1·8 | 2·3 | 1·2 | 1·8 | 1·4 | 2·6 | 1·8 | 3·3 |
| | 50 | 2·0 | 1·9 | 1·7 | 1·6 | 2·2 | 1·4 | 1·7 | 1·3 | 2·1 | 2·1 | 2·5 |
| | 65 | ca. 2·6 | 1·8 | 1·5 | 1·8 | 2·1 | 1·9 | 1·8 | — | 1·7 | — | 0·6 |
| | 80 | — | 2·0 | 1·5 | 2·5 | 2·8 | 3·1 | 2·3 | — | 2·3 | — | 0·2 |
| | 90 | — | 3·1 | 1·8 | — | 3·2 | 4·0 | 3·0 | — | — | — | 0·4 |
| | 100 | — | — | 2·3 | — | — | — | — | — | — | — | — |
| Dielectric constant | 5 | 2·66 | 2·63 | 2·62 | 2·66 | 2·72 | 2·73 | 2·74 | — | 2·92 | — | 2·60 |
| | 20 | 2·76 | 2·69 | 2·69 | 2·78 | 2·78 | 2·79 | 2·83 | 2·45 | 2·99 | 3·01 | 2·64 |
| | 35 | 2·81 | 2·76 | 2·76 | 2·86 | 2·89 | 2·82 | 2·90 | 2·49 | 3·16 | 3·09 | 2·75 |
| | 50 | 2·84 | 2·81 | 2·82 | 2·90 | 2·95 | 2·84 | 2·95 | 2·52 | 3·27 | 3·20 | 2·90 |
| | 65 | 2·87 | 2·85 | 2·86 | 2·92 | 3·00 | 2·86 | 2·97 | — | 3·30 | — | 2·91 |
| | 80 | — | 2·88 | 2·87 | 2·94 | 3·03 | 2·90 | 2·99 | — | 3·30 | — | 2·87 |
| | 90 | — | 2·90 | 2·88 | — | 3·06 | — | 3·01 | — | — | — | 2·84 |
| | 100 | — | — | 2·89 | — | — | — | — | — | — | — | — |
| Specific conductance $\times 10^{-12}\Omega^{-1}$ cm.$^{-1}$ | 35 | 1·1 | <0·1 | ≤0·1 | <0·1 | <0·1 | 0·12 | <0·1 | ≤0·1 | <0·1 | ≤0·1 | <0·1 |
| | 50 | 5 | 0·4 | <0·1 | 0·5 | 0·5 | 0·7 | 0·11 | <0·1 | 0·7 | <0·1 | 0·4 |
| | 65 | 50 | 2·6 | 0·3 | 2·9 | 2·4 | 3·6 | 0·7 | — | 11 | — | 2·9 |
| | 80 | — | 14 | 1·9 | 17 | 11 | 16 | 5·0 | — | 70 | — | 18 |
| | 90 | — | 38 | 5·8 | 50 | 34 | 35 | 13 | — | — | — | 41 |
| | 100 | — | — | 16 | — | — | — | — | — | — | — | — |

* In practice the total angle of loss is usually given; this is a disadvantage, in that the part of this angle governed by the loss due to ohmic conduction depends in quite a different way on the frequency than the part of the angle that is governed by the loss due to hysteresis.

The loss due to hysteresis, expressed in watts, may be calculated from (1); the tension $E$ is given in volts, and the capacity $C$ in cm.

Thus, if a condenser is used with a capacity of 100 cm. (with air as dielectric) and a tension of 20,000 volts is applied at a temperature of 90° C., there is, in the case of the above bitumen, a loss due to hysteresis

$$= \frac{2\pi}{9\times10^{11}} \times 50 \times 20{,}000^2 \times 100 \times 2{\cdot}88 \times 0{\cdot}018 \text{ watt}$$
$$= 0{\cdot}72 \text{ watt}$$

and a loss due to conduction (according to equation (2) and (4)) of 0·28 watt.

The total loss is about 1 watt. At temperatures below 70° C. none of the bitumens examined shows a higher loss (cf. Table III). When the plates are 1 cm. apart, the losses would, at a tension of 20,000 volts, even if no heat were transferred to the surroundings, increase the temperature of the bitumen by only 1½° C. per hour.

Thus, the losses are negligible if alternating voltage of low frequency is used.

The measurements further show that in the case of most of the bitumens examined the tan $\delta_H$, and therefore also the loss due to hysteresis as a function of the temperature, passes through a maximum between 20° and 40° C. At higher temperatures the losses due to hysteresis generally increase again. The ohmic losses, which may be ignored at room temperature, increase considerably with rising temperature, however; at temperatures between 70° and 100° C. (dependent on the consistency of the bitumen) the ohmic losses are already larger than the losses due to hysteresis.

At high frequencies of the alternating voltage, however, the loss due to hysteresis invariably becomes considerably larger than the ohmic loss, also at higher temperatures.

### C. Dielectric Constant.

As already said, the dielectric constant is also found when the angle of dielectric loss is measured. As the values given in Table III show, the dielectric constant increases with rising temperature, especially in the temperature range 20–50° C. This increase, which is closely connected with the maximum of the angle of loss, has no practical importance.

At the temperatures in question, the dielectric constants of the various bitumens lie between 2·5 and 3·3.

### D. Electrical Conductivity.

The conductivity was also determined by means of the apparatus sketched in Fig. 2, using direct current. From the capacity of the condenser found when the dielectric constant was measured, the cell constant of the condenser may also be deduced $\left[\text{cell constant} = \frac{1}{4\pi x \text{ capacity (in cm.)}}\right]$.

The cell constant is an apparatus constant which is equal to the product of the determined resistance and the specific conductance.

Therefore the specific conductance can be calculated from the cell constant and the resistance determined.

In the measurements the electric field strength was about 20 kv./cm.

The specific conductance (see Table III) increases considerably with rising temperature, and is generally higher the softer the bitumen; it is approximately proportional to the square of the penetration at a definite temperature.

R. N. J. Saal [4] has derived a relation between the penetration and the viscosity which can be approximated to:

$$\eta = \frac{c}{\text{pen.}^2}$$

($\eta$ = viscosity)
(pen. = penetration)

(strictly speaking, this equation applies only to bitumens which behave like purely viscous liquids); this means that the specific conductance is approximately proportional to the viscosity at a definite temperature; this is also to be expected on the strength of theoretical considerations.

For instance, in the case of bitumens harder than pen./25° C. = 40 the specific conductance at 20° C. $= < 10^{-15}$, at 50° C. $= < 7 \cdot 10^{-14}$. The softest of the bitumens examined (pen. 175) has the lowest value, viz. about $1 \cdot 6 \times 10^{-14}$ at 20° C. and $7 \times 10^{-13}$ at 50° C.

*References.*

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[2] G. W. Nederbragt, "World Petr. Congress," Paris 1937, Vol. II, chap. II, p. 653; *Archiv. f. techn. Mess.*, 1937, V, 943.
[3] British Standard Specification for bituminous filling compounds for electrical apparatus, No. 688—1936.
[4] R. N. J. Saal, *J. Instn Petrol. Tech.*, 1933, **19**, 176; "World Petr. Congress," London, 1933, II, p. 515.

# SOME EXPERIMENTS ON SEIZURE BETWEEN LUBRICATED HARD STEEL BALLS.*

By D. Clayton, B.Sc.


## Summary.

Experiments have been made to find the effect of change of the test conditions on the behaviour of lubricants in the 4-ball apparatus. In tests with a continuously increasing load, the breakdown loads for mineral and fatty oils were 40 per cent. higher than in tests at a series of constant loads, and rather more for an extreme-pressure lubricant; the wear values corresponded with those found in previous tests for the particular loads. The scatter of the results, however, prevented this method of loading being used to obtain a shorter test than the normal. Tests at half and double the normal speed showed that with increase of speed the breakdown load decreased, the time to seizure decreased, and the wear generally increased. Interrupting the seizure with a mineral oil by removing the load showed that most of the wear occurred in the early part of the seizure period; on restoring the load, even after several minutes, the friction immediately rose to its high value again. This test showed that the continuance of high friction with this type of oil was not merely due to high temperature at the contact persisting from the early part of the failure. Considerable increase of load could be made after recovery before a second seizure resulted. Finally experiments are described showing changes of seizure behaviour due to rigidity of the ball-chuck mounting, and mention is made of a change in the loading system of the apparatus.


## Introduction.

Results of an investigation into the effects of a fairly comprehensive series of lubricants on the seizure characteristics of hard steel balls have previously been published.[1-3] In this work, for which the 4-ball apparatus was used, the standard conditions were maintained throughout. Some experiments have now been made to find the effect of varying the conditions of test—*e.g.*, the speed has been varied, an increasing load test has been tried, the seizure has been interrupted, and the rigidity of the chuck mounting has been varied. This work has been carried out primarily with the ultimate aim of providing information on the phenomenon of seizure, but also for the thorough investigation of a testing apparatus which has a number of good features; in the latter connection Blok[4] has made important claims as to its advantages from the point of view of contact temperature as a criterion of failure in gearing, and as regards correlation with hypoid gear behaviour.

The apparatus and its normal mode of use have been described by Boerlage[5] and in the previous papers. Only the following brief account is therefore given. A $\frac{1}{2}$-in.-diameter hard steel ball is rotated under load in the cavity between three other similar balls clamped together in a cup containing the lubricant. Tests are normally made at each of a series of loads, the speed being 1500 r.p.m. (113 ft./min., 58 cm./sec.). A friction–time chart is autographically recorded, showing the friction behaviour during seizure. The wear is represented by the mean diameter of the circular impressions worn on the three clamped balls. The Hertz line on the wear diagrams shows the elastic deformation. The breakdown load is that

* Paper received 26th October, 1939.

at which seizure first occurs in the course of the one-minute run; it is shown by the line joining the two portions of the wear–load curve.

### Tests with a Continuously Increasing Load.

In a number of extreme-pressure lubricant testing machines the load is increased either continuously or in steps during each test, and it was thought that it would be interesting to see how this method of loading affected the behaviour of lubricants in this apparatus. If consistent results were obtained, much of the information at present provided by tests at each of a series of loads would be available from a single test; thus there would be a breakdown load, which would be influenced to some extent by properties of the lubricant affecting the time to seizure in the usual tests, and the friction–time chart would show the nature of the seizure, giving the maximum coefficient of friction and the time to recovery.

Experiments were made with three oils, one of each of the main kinds available—viz., B.P. paraffin to represent the mineral oils, castor oil to represent the fatty oils, and E.P. oil D to represent the extreme-pressure lubricants of the kind containing sulphurized fatty oil. The weight-carrier on the loading-lever of the apparatus was replaced by a suitable container into which lead shot was run. Owing to a tendency for the loading-lever to bounce on starting at zero load, an initial load of 20 kg. was imposed. The shot stream was cut off as soon as seizure occurred, and the apparatus was stopped after 1 minute total running time.

Starting with a loading rate of 7 kg./sec., the results with B.P. paraffin and E.P. oil D were quite consistent, the breakdown loads being 57½–63 kg. (mean 61), and 165–177 kg. (mean 171), respectively. With castor oil, however, there was a wide scatter, most of the results lying within the range 90–110 kg., but some extending to 140 kg. The experiments were continued to find whether there was any influence due to the rate of loading, rates of 2½ and 5 kg./sec. being used. The mean loads were only a little different, but there was a rather greater scatter.

The diameters of the wear impressions due to seizure varied with the breakdown loads, and corresponded with those obtained in the normal method of test for these loads. This is shown by Fig. 1, in which the mean curves from previous tests have been copied, and are seen to run through the present plotted points as nearly as the mean curves usually represent the results. This agreement would be expected to the extent that once material began to be removed from the lower balls the behaviour would be the same as in the previous tests.

Representative friction–time charts are shown in Fig. 2. The times to recovery and the maximum coefficients of friction were generally similar to those in normal tests.

Taking all the results into account, the mean breakdown loads are 60, 107, and 165 kg. for B.P. paraffin, castor oil, and E.P. oil D, respectively, compared with 43, 75, and 100 kg. by the normal method of test. The increase due to some of the time element of the normal test being expressed as load in this test, leaves the relative values for B.P. paraffin and castor oil practically unchanged, but the new value for E.P. oil D is relatively

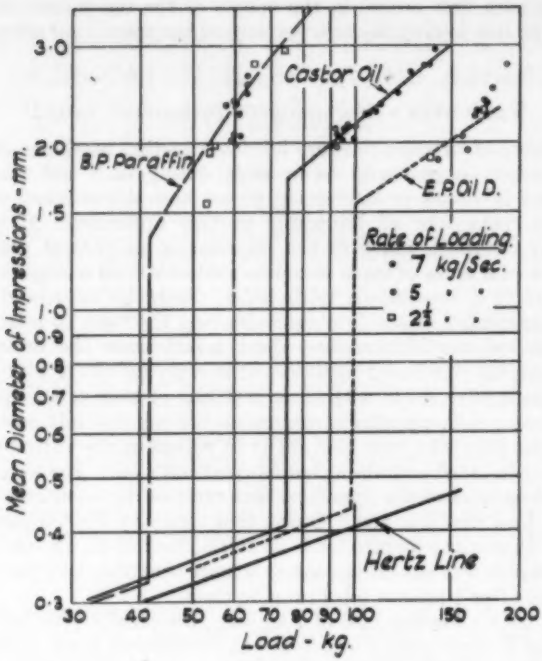


FIG. 1.

WEAR-LOAD DIAGRAM FOR INCREASING LOAD TESTS.

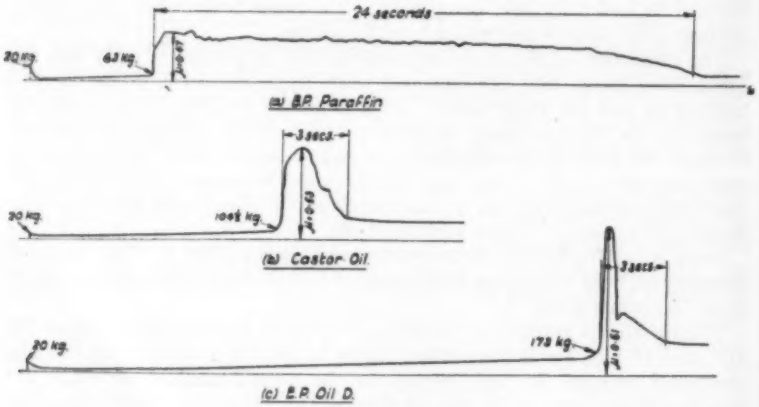


FIG. 2.

FRICTION-TIME CHARTS FOR INCREASING LOAD TESTS.

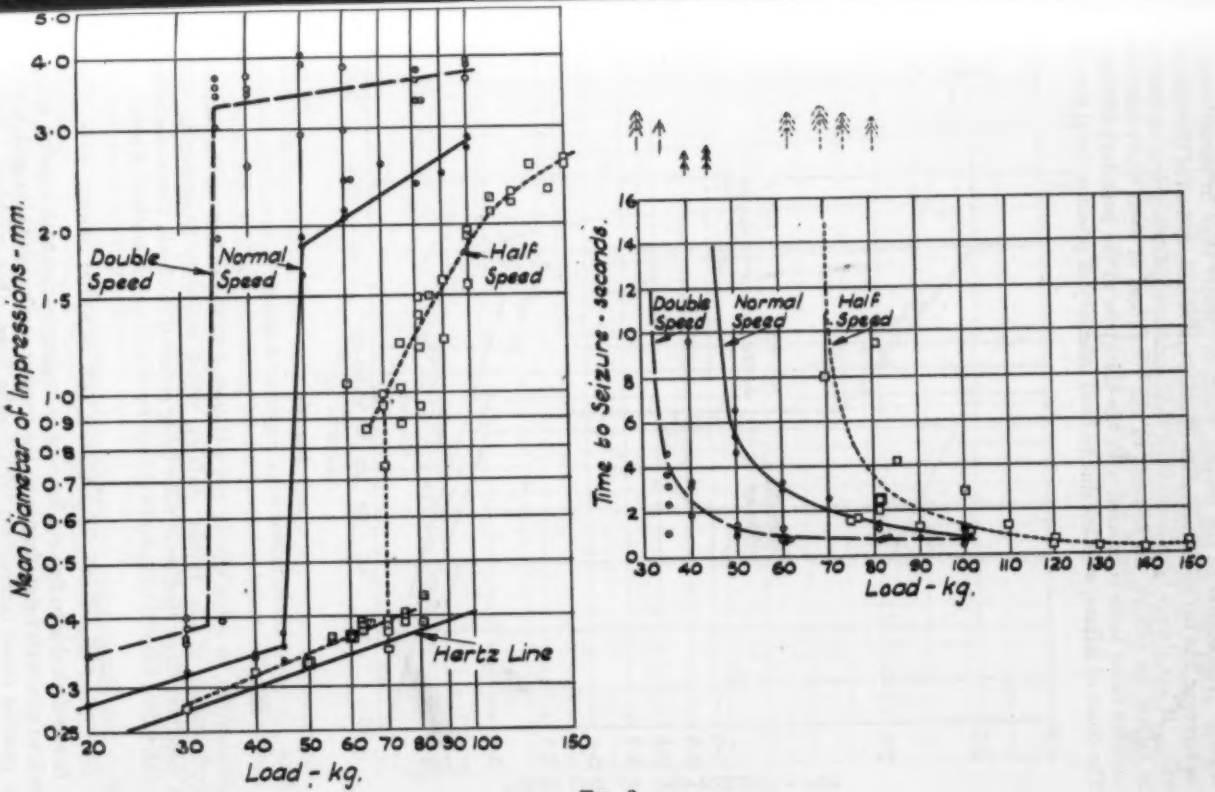


FIG. 3.

MINERAL OIL K1 : TESTS AT 3 SPEEDS.

higher. The scatter of the results, which is greater than in normal tests, is, however, the bar to the adoption of this type of test instead of the normal one. It has always been considered that some inconsistency was inevitable in failure by seizure, on account of the roughness of even finely-finished surfaces being large compared with the thickness of the boundary oil film. The onset of failure, whether due to local intensity of pressure, local rise of

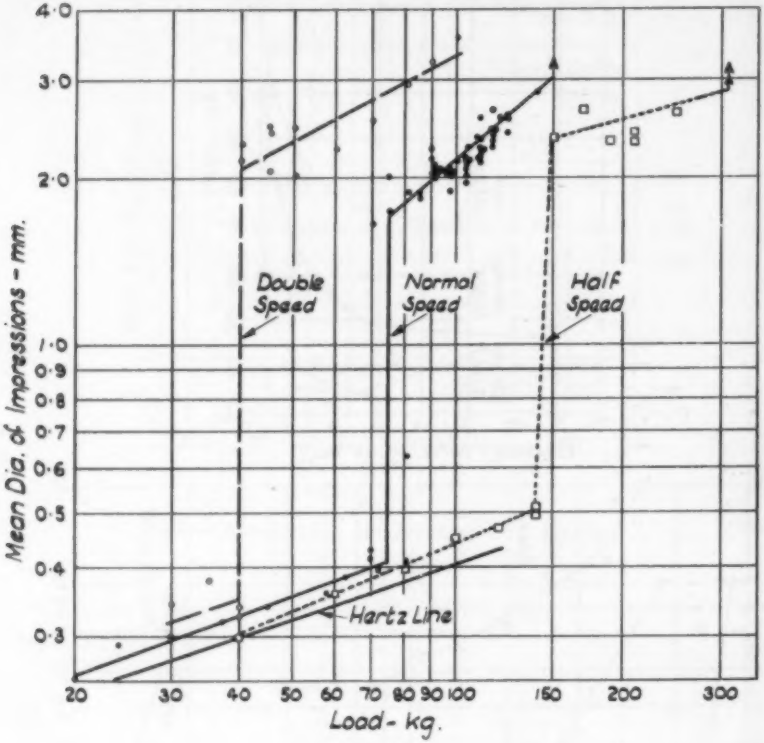


FIG. 4a.

CASTOR OIL : TESTS AT 3 SPEEDS.

temperature, or other effects, must therefore be dependent on the relative configuration of the contact surfaces, which will vary from test to test. A relatively large number of tests being required to obtain a representative mean value, there is little to be gained by changing the method of test.

## THE EFFECT OF VARYING THE RUNNING SPEED.

It was desirable to find out how the behaviour varied with running speed, both to give wider significance to the present results, and also with a view to possible closer comparison with results from other machines. Pulleys

half and twice the normal size on the motor spindle drove the top ball of the apparatus at half and twice the normal speed of 1500 r.p.m. (113 ft./min.). A thin spindle oil, K1, was chosen to represent the mineral oils, and castor oil the fatty oils; the results as regards time to seizure and wear are shown in Fig. 3 and in Figs. 4*a* and 4*b* (the scales of the latter are

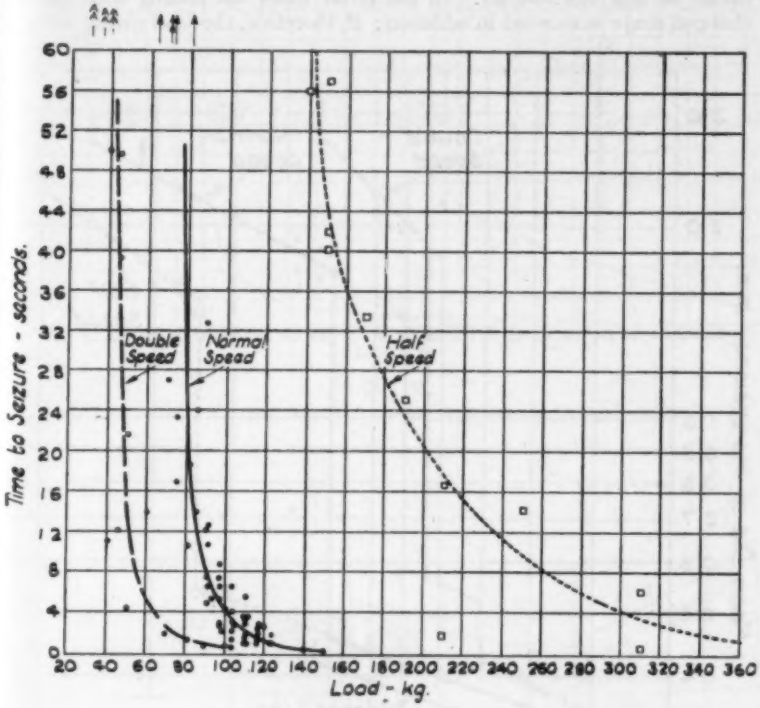


FIG. 4*b*.

CASTOR OIL: TESTS AT 3 SPEEDS.

different from normal). E.P. oil B1, Figs. 5*a* and 5*b*, represented the extreme-pressure lubricants of the kind containing a sulphurized fatty oil, and E.P. oil E, Fig. 6, those containing lead soap and sulphur. In the seizing time–load diagrams the arrows near the top indicate that in these tests there was no seizure within the 60 seconds of the test; where a number is added this shows the number of seconds to seizure, the point falling beyond the limit of the diagram. The vertical arrows in the wear–load diagrams indicate that a welding seizure occurred at that load.

The behaviour of the apparatus at double speed was generally not very satisfactory. There was a tendency to set up vibration, and the friction–time charts were very irregular and variable from test to test; consequently there was rather greater scatter of the wear results, and to some extent of the times to seizure, than at lower speeds.

For the first three lubricants increasing the speed reduced the breakdown load, decreased the time to seizure, and increased the wear. Considering that the speeds were in a geometric progression, it is apparent that the influence of decrease of speed from normal to half on breakdown load and time to seizure was disproportionately large; this was particularly so with castor oil and E.P. oil B1. In the latter cases the seizing time curves changed shape somewhat in addition; if, therefore, the load giving seizure

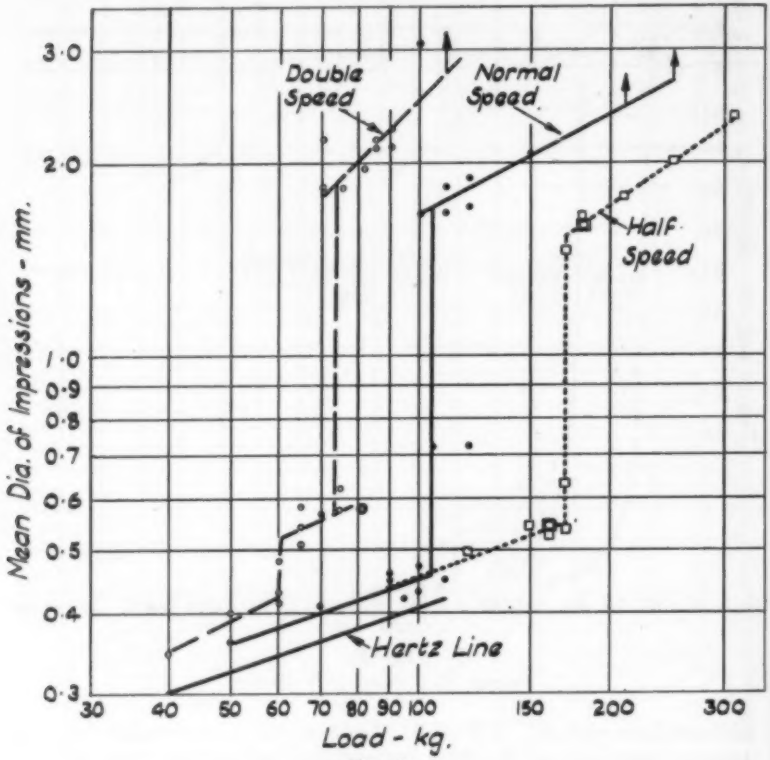


FIG. 5a.

E.P. OIL B1 : TESTS AT 3 SPEEDS.

in 2½ seconds were to be adopted as the breakdown load for gear lubrication, as suggested by Blok [4] and discussed in a previous report,[2] the value at half speed would be particularly high. The influence of decrease of speed on the wear with seizure was most marked with the mineral oil. Similarly the effect on wear without seizure was greatest with this oil, the distance from the Hertz line of the mean line for these conditions being greater with increase of speed. This was partly due to the greater linear travel in the 1 minute of the test at higher speeds, but it was probably influenced also

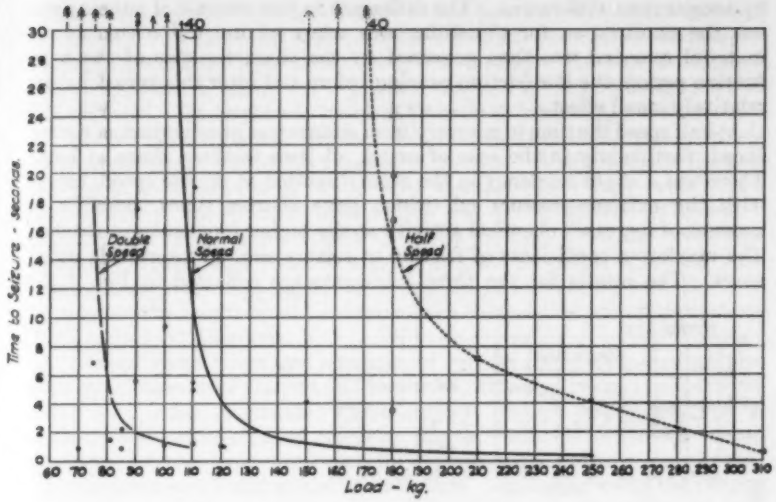


FIG. 5b.

E.P. OIL B1 : TESTS AT 3 SPEEDS.

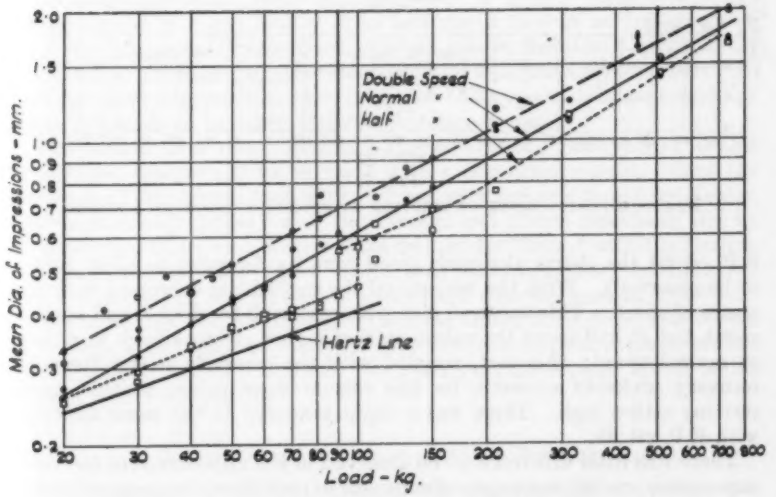


FIG. 6.

E.P. OIL E : TESTS AT 3 SPEEDS.

by temperature differences. The difference in the amount of rubbing was not the explanation for the differences when seizure did occur, as the material removed was then governed by the characteristics of the high-friction period, the low-friction running before and after this period having relatively small effect.

At half speed the time to recovery from seizure was greater than at normal speed, particularly in the case of castor oil (two to three times as long). There was a slight tendency in the same direction at double speed, except with the extreme-pressure oil, which gave shorter times, possibly on account of increased chemical activity at the higher temperatures reached. The maximum coefficients of friction at seizure showed interesting differences. The results for the three lubricants are collected in Fig. 7 (for

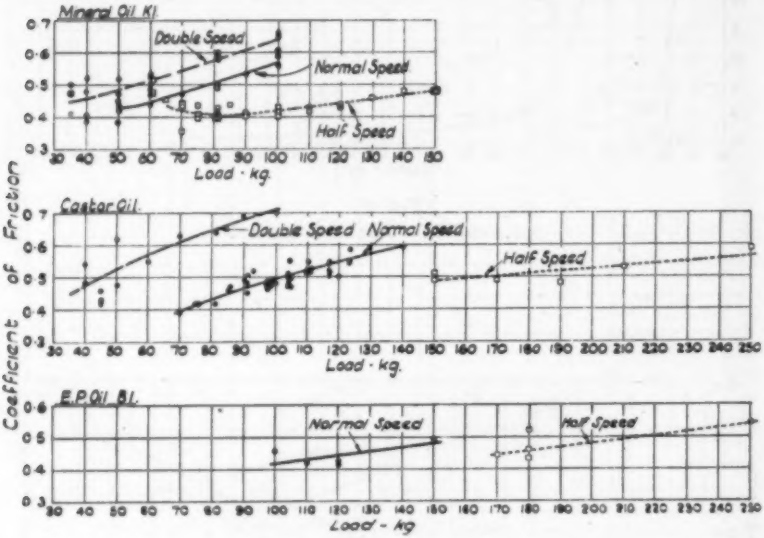


FIG. 7.

MAXIMUM COEFFICIENTS OF FRICTION AT SEIZURE : TESTS AT 3 SPEEDS.

E.P. oil B1 the charts at double speed were too irregular to allow values to be observed). With the mineral oil the coefficients decreased with decrease of speed. This occurred also with castor oil for double and normal speed, but at half speed the values started higher at breakdown load than at normal speed; this fact, coupled with the generally longer times to recovery probably accounts for the seizure wear values at this speed starting rather high. There was a slight tendency in the same direction with E.P. oil B1.

There was little difference to be observed in the appearance of the wear impressions, except more signs of softening or melting of the metal at double speed; the impressions tended to be smoother, and there were " fins " of metal at the trailing edges.

*Lead Soap–Sulphur E.P. Lubricant.*—It had been found in tests at normal speed that E.P. oil E of this type behaved differently from other lubricants.[2] Instead of breakdown at a certain load, with a sudden increase of diameter of wear impression, there was a gradual increase of wear throughout the range of loads. The wear was appreciable even at low loads, but extremely high loads could be taken without the welding seizure occurring which would be the result with other types of lubricants. A slight rise of friction occurred at moderate loads, but it never increased to a high value. The same behaviour was found in tests at half and double speeds. The wear–load diagram for all three speeds is shown in Fig. 6. There were not enough observations of time to rise of friction to enable a satisfactory diagram to be produced; as, however, this rise of friction was not like that at a seizure, the results would not have been comparable with the previous seizing time–load diagrams.

At normal speed there was a change of type of impression through the following succession of stages: (1) a smooth, flat impression, typical of no seizure with other lubricants; (2) a smooth, cupped impression; (3) a rough, scored impression of irregular shape; and (4) a scored, round impression of the type produced by seizure with ordinary lubricants. This transition was found at the other speeds. At double speed the ranges overlapped each other, and there was again no break in the curve; at half speed, however, there was a definite break at 100 kg., at the change between the first two types of impressions. The slight changes of friction were first observed in all cases when smooth wear gave place to scoring wear.

In contrast with the other lubricants, the friction–time charts at double speed were smooth with E.P. oil E. The maximum coefficients of friction were constant at each speed over the range of loads, and, though the differences were small, there appeared to be a definite trend downwards with increase of speed from 0·12 at half speed to 0·10 at double speed. This result is probably associated with the greater chemical activity of the lubricant at the higher temperatures obtained with more severe conditions; this has been suggested as the reason for this type of lubricant enabling very high loads to be taken without welding occurring.

*Comparison with Other Results.*—The results described above enable qualitative comparison to be made with a few other results. Thus the decrease of breakdown load with increase of speed was found by McKee, Harrington, and McKee[6] with the Timken and Almen machines, and by Southcombe, Wells, and Waters,[7] and by van der Minne,[8] with the Timken machine. In the third paper it was also confirmed that the difference between the fatty and mineral oils increased with decrease of speed. In both the second and third papers the wear before breakdown was shown to be high with a lead soap–sulphur type of lubricant; the same result has been found in this investigation, particularly at the highest speed, which is most nearly comparable.

## Examination of the Stages of Seizure.

In order to throw light on the mechanism of seizure and recovery, a few experiments have been made in which the normal procedure in individual tests has been varied.

*Short Running Times.*—A general trend towards higher wear had been noticed when the time to recovery was greater. Although it was apparent that the increase of diameter was not by any means proportional to the time at high friction, it was desired to check this observation more definitely; some tests were therefore made in which the load was taken off the balls soon after the rise of friction at seizure. A thin mineral spindle oil (like that K1 already referred to) was used, the machine running at its normal speed of 1500 r.p.m. In the first tests at 60 kg. the average time to recovery was 20 seconds, and the wear impressions were 1·87 mm. diameter. Taking off the load after 4 seconds of high friction, the wear impressions were 1·53 mm. diameter. This confirmed that the rate of increase of size fell with continuation of the high-friction running. The rate of change of diameter becomes smaller at higher values for the same amount of material removed, but, calculating the volumes involved, the wear was even so only doubled for a five-fold increase of time. A similar result was obtained at 90 kg. The normal time to recovery was 30 seconds, the wear impressions 2·72 mm. diameter; taking the load off after 5 seconds, the wear impressions were 2·25 mm., and the volume worn away was halved.

Comparing these results with those for castor oil, it is apparent that for periods corresponding to the times to recovery of castor oil the wear would be approximately the same, indicating a similar initial rate of wear.

*Interrupted Seizures.*—The time to recovery was in these tests characteristic of the oil. No definite explanation of the mechanism of recovery had been found, but there was apparently a re-establishment of some kind of effective lubrication. The surface of the impressions was too rough to allow a complete fluid film to be formed. Rather was it probable that, first, the increase of size of impression led to wider distribution of the points of contact, so that both by lowering the average load on each and by separation, the maximum temperature reached fell; at the same time the roughness allowed access of the oil, so that by further cooling and the formation of boundary films a balance was re-established between heat generated by friction and heat carried away by conduction and by the oil. The high-friction phase was particularly persistent in the case of the mineral oils, and yet, as had been shown, the major portion of the wear occurred in the first few seconds. This pointed to a delay on the part of the oil in performing the second function described. It seemed that information on this score would be provided by temporarily removing the load to allow flooding of the contacts by the oil, thus cooling and adequately lubricating them.

Tests were made at 60 kg. with the same mineral oil as in the previous tests. It was found that when either momentary (1–2 seconds) or long (5 minutes) intervals were allowed, the friction immediately rose again to its normal value on re-imposing the load, and approximately the same total time of high friction was completed. The time before interruption varied from 2½ to 11 seconds out of total times of 14–23 seconds. In one test there were three breaks, but in each case the friction rose again, to complete 15 seconds total time at high friction before recovery.

It is apparent, therefore, that the continuance of high friction running was not merely a question of high temperature at the contact persisting from the early part of the failure, or of the lack of opportunity for oil to

form a boundary film; the result points to it being governed critically by the surface condition, either roughness or possibly the condition of the metal.

*Load Increased after Recovery.*—Under the same conditions as before, further load was added after recovery in order to discover how stable a state was reached. No change was found for 16 and 32 kg. extra. With 40 kg. extra, further seizure was obtained on two occasions, and no seizure on another. When, however, the load was added especially carefully, no further seizure was obtained on three occasions. With 56 kg. extra there was one non-seizure and one seizure, and with 80 kg. a seizure. The increments in the load were made at about 4 seconds after recovery.

The second seizure was similar to the first one, but the coefficient of friction was higher; it was not quite as high, however, as that corresponding to normal seizure at the higher load. Recovery occurred again in the usual manner, and the final sizes of impressions were nearly the same as would have been obtained in normal seizures at the higher loads. When no further seizure occurred, the wear impressions were still within the range of values for normal seizures at 60 kg., but the average was a little higher.

It is thus apparent that the state after recovery is one of marked stability, considerable additional load being required to cause further seizure.

## Investigation of the Chuck Mounting.

At this stage, owing to failure of the chuck to hold the top ball tightly, a new chuck had to be used. It was found, however, that somewhat different results were obtained. For example, in tests of a mineral oil an unusual number of mild seizures were obtained in the neighbourhood of the breakdown load, and on a number of occasions a vibration started, causing the loading-lever to bounce. The arrangement of the chuck is shown in Fig. 8. It has a plain portion *A* which enters the driving spindle *B* of the apparatus, and is held by a taper pin *C*. It was found that with the new chuck the collar *D* was just out of contact with the end of the spindle, so that the load was coming entirely on the pin. Fitting a washer made the chuck rigid with the spindle when the pin was driven in, and resulted in behaviour which was again rather different. A number of experiments suggested that the differences were due to the elasticity of the system, leading to a series of tests in which the washer thickness was decreased in steps, giving a gradual transition from rigidity of the chuck to maximum freedom with the load coming entirely on the pin.

Fig. 9 shows the succession of time charts obtained with castor oil at 100 kg. (The charts for thicknesses 0·033–0·029 in. were similar to that for 0·035 in., except that additional kicks occurred later in the chart.) The behaviour was consistent with explanation on the following lines. The loading system being somewhat elastic and not heavily damped, there was some tendency for the balls to separate momentarily when the sudden rise of friction occurred at seizure. The hole in the portion *A* of the chuck was large and made contact only at the centre of the length of the pin, thus giving some freedom and elasticity in torsion. With no friction at the washer there was thus opportunity for the twisting movements of the chuck to combine with the freedom of the loading system to give fluctu-

ating contact loads at the balls, and thus a ragged chart. Thicker washers, however, introduced friction at the collar *D* to resist and damp twisting of the chuck; the breaks in the charts therefore occurred at higher friction loads, and there was less tendency to maintain movements of the loading system. A completely smooth chart was eventually obtained, but still

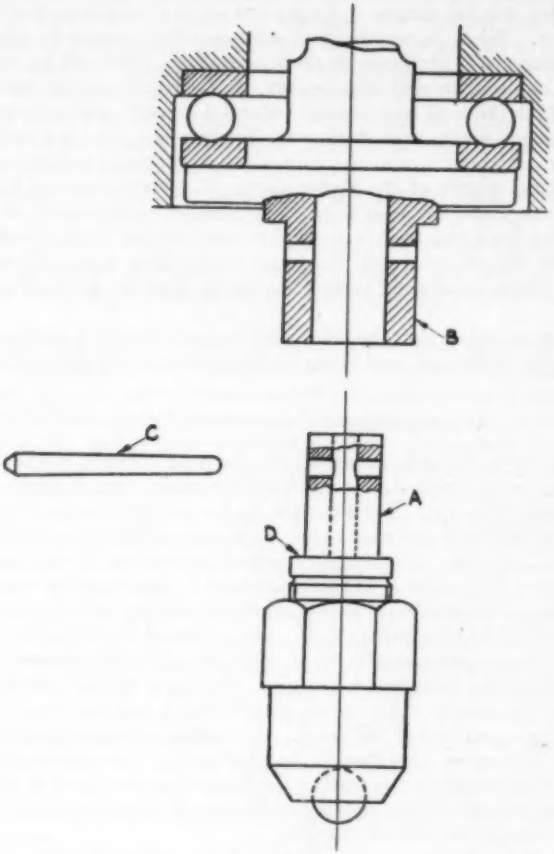


FIG. 8.

BALL CHUCK MOUNTING.

thicker washers made the chuck rigid, and movement could then only occur in the loading system; at this particular load the relief thus obtained was sufficient to prevent the seizure proceeding, the wear impressions being therefore small, 0·7 mm. diameter, compared with 2·1 mm. for normal seizure. At smaller washer thicknesses the wear remained constant, showing that the breaks in the charts did not affect the wear, or that the longer time to recovery compensated for any such effect.

These results were confirmed by modifications to the old chuck and also by experiments with the new chuck in which a new hole was drilled and taper-reamered to fit the pin.

The washer thickness giving behaviour like that with the old chuck was 0·027–0·026 in. This old chuck had been used for all the work previously carried out, and the results so far published are thus all comparable. It seemed desirable, however, to obtain results with the rigid chuck, this being the condition most easily established with certainty. The times to seizure with the mineral spindle oil K1 and castor oil were consistent, and agreed closely with those previously obtained, but the wear curves were

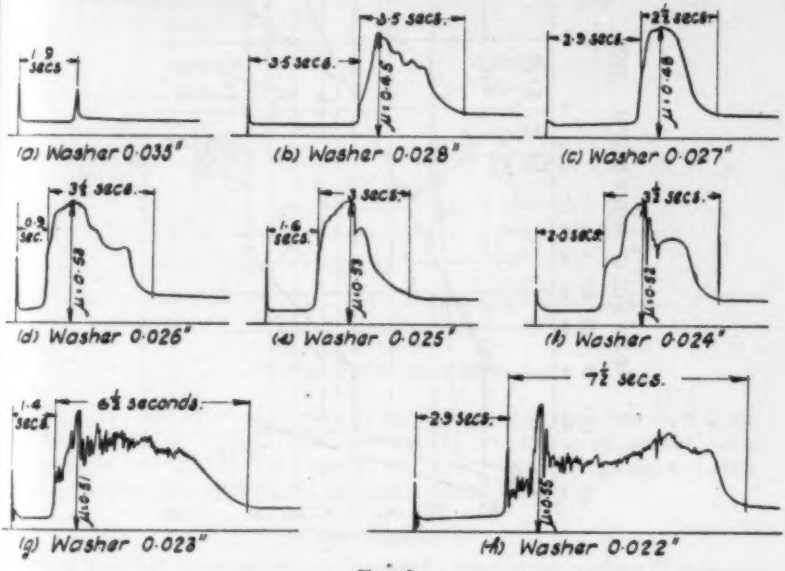


FIG. 9.

EFFECT OF WASHER THICKNESS, CASTOR OIL. 100 KG.

different. Fig. 10 shows that instead of a sudden change at the breakdown load to consistent seizures, mild seizures were first obtained. They began at a slightly lower load, and, in the case of the mineral oil, gradually increased in severity with increase of load. With the fatty oil mild seizures were obtained over a range of loads, and then there was a sudden change to more normal ones. The charts for the high loads were in each case rather more broken than in the usual tests, and for castor oil the maximum coefficient of friction averaged 0·65, an unusually high value. For the mineral oil the coefficient was generally 0·25, but at the highest loads parts of the charts reached the higher values usually found.

Somewhat similar curves to this for castor oil were obtained by van Dijck and Blok [9] and van der Minne [8] for fatty oils in this apparatus. It is probable, therefore, that the chucks which they used were more rigid than those used for the previous tests in this case.

Although the effects of differences of rigidity are not perhaps very serious in this case, in that the times to seizure are unaltered and the relative order of the oils is unaffected, these experiments show that the elasticity of the system has an appreciable effect on the behaviour, and it may be that this factor is one contributing to differences of behaviour in different testing machines. If tests are made under a single set of conditions without a

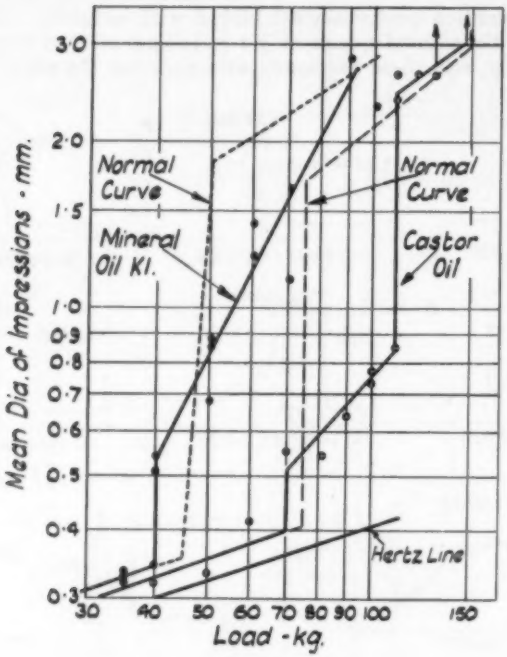


FIG. 10.

TESTS WITH THE CHUCK RIGID.

complete exploration, it is apparent that unusual differences could be found. Baxter, Snow, and Pierce [10] have described how change of the operating conditions of a Timken machine altered the type of seizure obtained, in particular the occurrence of a seizure of the type described above as mild. The behaviour in vehicle back-axles and other practical mechanisms would doubtless be affected similarly.

### CHANGE IN DETAIL OF LOADING SYSTEM.

Brief mention may be made here of a change made in the loading system. When preliminary work with this apparatus had shown that an extended programme of tests might usefully be undertaken, the loading system was checked for accuracy. It was then found that there was a relatively large friction force at the top face of the mushroom-shaped piece *A*, Fig. 11*a*,

which transmitted the load from the lever to the column under the ball-cup. As the loading-lever was lowered this face had to slide a little along the under-face of the buffer *B*, and the friction force acting above the level of the fulcrum reduced the operating load by 5 kg. or more at 40 kg. loading. The mushroom was therefore replaced by a conical-ended strut, as shown

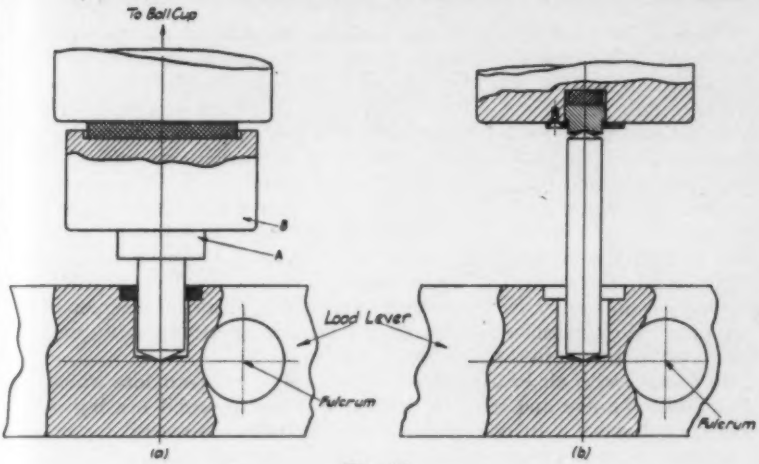


FIG. 11.

DETAILS OF LOADING SYSTEM.

in Fig. 11*b*; the effect of friction in the system was then less than ½ kg. at 40 kg., 1 kg. at 100 kg. The loads were 1½ per cent. small, probably due to a slight error in the short arm of the lever. This change did not alter the behaviour described in the previous section.

## ACKNOWLEDGMENT.

This work has been carried out as part of a general programme of research in lubrication in the Engineering Department of the National Physical Laboratory, and the author is indebted to the Director for permission to publish this paper. Acknowledgment is also made of the assistance of Messrs. M. J. Wilkie, B.Sc., and B. W. J. Greig in carrying out the tests.

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# HAZARDS ASSOCIATED WITH BUTADIENE AND ITS PEROXIDES.*

By D. A. Scott.†

Certain information concerning unusual hazards which may be encountered in working with butadiene and related compounds has come to our attention, and we take this opportunity to pass it on to any who may find it useful.

Butadiene, when heated under pressure, may undergo violent thermal decomposition. In one instance, explosive decomposition with carbon formation occurred on heating butadiene in a stainless steel bomb, while previous experiments of the same sort had been carried out without any unexpected occurrences. It has been suggested that sufficient material had been placed in the bomb so that on heating it became entirely filled with liquid, and that the hydrostatic pressure may have initiated a decomposition similar to that which takes place in acetylene upon compression. No explosions resulting from heating at atmospheric pressure have been observed in the absence of oxygen.

In contact with air or oxygen, butadiene may form peroxides which are violently explosive and may be detonated either by mild heating or by mechanical shock. In one instance solid butadiene, exposed for only a very short time to oxygen at sub-atmospheric pressure, absorbed sufficient oxygen so that on warming slightly above the melting point a violent detonation occurred. It is suspected that the behaviour of butadiene in this respect is influenced strongly by the accidental presence of oxidation catalysts or inhibitors. The addition of an inhibitor to butadiene which is to be distilled or allowed to stand, even at very low temperatures, in contact with air or oxygen would help to avoid an accidental explosion.

After emptying a storage tank of crude butadiene some polymer was found in the bottom of the tank. The polymer contained 0·095 equivalents of peroxide oxygen per 100 gm., and could be detonated easily by a hammer blow. The polymer containing the oxygen compounds was insoluble in the butadiene, and the butadiene itself contained only a trace of peroxides. The peroxides were probably formed by reaction between butadiene and air. Subsequent investigation showed that the peroxide could be destroyed safely by treatment with strong caustic soda (48° Be; 47 per cent. NaOH). Thus butadiene might be conveniently freed of peroxides by storage over caustic or by passage through a caustic wash.

* Received 3rd April, 1940.

† Shell Development Company, Emeryville, California.

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